4th International Conference on Recycling and Reuse

Book of Abstracts

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RECYCLING AND REUSE, 2018

4th INTERNATIONAL CONFERENCE ON RECYCLING AND REUSE

BOOK OF ABSTRACTS

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Preface

International Conference on Recycling and Reuse (R&R, 2018) organized by one of the leading universities of Turkey; Istanbul University-Cerrahpasa, was held in Istanbul, 24-26 October, 2018. The conference brought together engineers, scientists, practitioners and other environmental professionals from many countries all over the world to exchange emerging ideas and to investigate key issues such as: integrated waste management; novel applications for reuse and recycling; renewable energy sources and green technologies. Over 100 oral and poster presentations as well as eight plenary lectures and six invited talks from eminent researchers have been scheduled in an intensive three-day program. Most importantly, over 40 young master and doctoral students participated in the conference. The participation of about 20 young researchers was subsidized by R&R, 2018 organization through fee remission.

The organizers would like to express their thanks to the keynote speakers for their excellent presentations. Special thanks should also be addressed to the members of the Scientific Committee. Moreover, we are very grateful to the members of the Organizing Committee as well as to our Sponsors who made the R&R, 2018 Conference a great success. It is also worth to mention that presented contributions, both oral and posters, could be submitted as full research papers to the journals; Desalination and Water Treatment, International Journal of Global Warming, International Journal of Hydrogen Energy, Journal of Hazardous Materials, European Journal of Chemistry, Environment and Engineering Sciences, International Journal of Agriculture, Environment and Food Sciences which provided special efforts to publish the selected conference papers. Finally, we thank all participants without whom the R&R, 2018 Conference would not have been possible.

We would like to welcome you at the forthcoming 5th International Conference on Recycling and Reuse (R&R, 2020).

Hoşçakalın,

October 2018, Istanbul

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Table of Contents

Preface iii
Committees iv
Table of Contents vii

ORAL PRESENTATIONS 1

Utilization of Lime, Gypsum and Cement as an Additive Material in Liner System
K. Dincer, S. Y. Guvenc, G. Varank 2

Do we really need to remove trace pollutants from wastewater? An innovative assessment approach
G. Bertanza 5

Release of Metals and Nutrients during Sewage Sludge Hydrolysis by Rhamnolipid and Saponin
A. Uysal, E. Celik 7

Enhanced Solar-Driven Water Splitting of 1D Core-Shell Silicon-Metal Oxide Nanopillars
I. Iatsunskyi, K. Siuzdak, M. Pavlenko 9

Elimination of Antibiotic Resistance at Urban Wastewater Treatment Plants by Iron-based Heterogeneous
Advanced Oxidation Processes
I. Arslan Alaton, A. Karatas, Ö. Pehlivan, T. Ölmez Hanci 11

The Potential of Water Saving in Buildings: Greywater Reuse
N. Büyükkamacı, E. Bağcılar 13

Effect of Phosphate on Anammox Process
İ.Ç. Erdem, B. Çalli 15

Evaluation of Municipal and Petrochemical Industry Sludges as a Feedstock for Biodiesel Production:
Effect of the Acid and Combined Acid/Microwave Pre-treatments
D. Alper, E. Babayiğit, A. Erdinçler 17

Industrial and Agricultural Wastes as a Potential Biofilter Media for Groundwater Nitrate Remediation
E. B. Özkaraova, R. M. Kalin, S. Gkionzepas, Charles W. Knapp 19

Hexavalent Chromium Removal Using Ion Exchange (IX) Enhanced Capacitive DeIonisation (IX CDI)
H. Senoussi, K.E. Bouhidel 21

Preliminary Assessment of Durian Peel Liquid Smoke Utilization as a Natural Preservatives for Mackerel
M. Faisala, A. Gania, F. Mulanaa 23

Ammonia Recovery From Chicken Manure Digestate via Gas Diffusion Tubular Polypropylene
Membrane
A. Bayrakdar 25

Sepiolite Supported Co-Co-B Catalyst for Hydrogen Generation from NaBH₄
S. Hosgün, M. Özdemir 26

State-of-the-art Technology for the Stabilization of Pb in the Incineration Fly Ash Using Waste Fishbone
Hydroxyapatite
A. Saffarzadeh, M. Nag, T. Nomichi, T. Shimaoka 28

Classification and Determination of Drinkability of Thermal Waters in Erciş and Çaldıran (Van, Turkey)
H. Düzen 30

Recycling of gallium from gallium nitride waste of LED industry by hydrometallurgical method
Li-Lin Hsu, Wei-Sheng Chen 32

The Effect of ZrMOF Types on Gas Permeability Properties of PEBA Mixed Matrix Membranes
Y.B. Ilgaz, S.Deniz 34

ZrO₂ supported on Bamboo Leaves Ash as Heterogeneous Catalyst in Microwave-Assisted Biodiesel
Conversion
I. Fatimah, D. Rubiyanto, A. Taushiyah, F.B. Najah, U. Azmi, Y. Sim 36

Enhancing the effectiveness of methylene blue (MB) phodegradation by ion Cu²⁺ doped to magnetic-
photocatalyst (Fe₃O₄/TiO₂)
M. M. Musawwa, E. S. Kunarti, Sutarno 38

vii
Removal of Cu(II) ion from aqueous solution by activated carbons produced from banana fruit bunch (Musa paradisiaca)  
Allwar Allwar, Ade Setiawan, Hendra Agitya Ermawan, Tomy Alviansah 41

Optimization of Dilute Acid Hydrolysis of Kitchen Wastes for Bioethanol Production  
M. N. Kerimak Öner, S. Fersiz 43

Environmental Sensitivity of Printed Circuit Board (PCB) Manufacturing to Transportation, Cu Recycling Rate and Energy Source Variations  
E. Özkan, B. Bas, N. Elginoz, F. Germirli Babuna 44

Production of Levulinic Acid From Biomass With Using Recyclable Magnetite Solid Acid Catalysts  
B. Kaya Össel, B. Niş, D. Öztürk 45

Shale gas extraction by hydraulic fracturing and flowback treatment technologies from shale gas extraction: A review  
H. Sari-Erkan, N. Bakaraki-Turan, G. Onkal-Engin 46

Synthesis of the Iron Nanoparticles by Using Pinus brutia Extract and Hydrogen Gas Production During the Synthesis  
D. Uzunoğlu, A. Özer 47

Effect of Seed Biomass on Wastewater Treatment Performance  
E. Demirkaya, H. Unver, B. Ciftcioğlu, G. Ozyildiz, G.E. Zengin, I. Pala-Ozok, E. Cokgor, D. Okutman Tas 49

Synthesis and Characterisation of Silica gel 60 Supported Iron-Zinc Bimetallic Nanoparticles for the Adsorption of Malachite Green  
F. Toprak, F. Karanfil, D. Uzunoğlu, M. Ergütt, A. Özer 51

Treatment of Pharmaceutical Wastewater by Combination of Electro-Fenton, Electrocoagulation and Photocatalytic Oxidation Processes  

Study Total Synthesis Of Natural Anti-Marine Fouling Agent (Synthesis of 7th Intermediate Compound From Omaezallene Derivative)  
N.I. Prakoso, T. Umezawa, F. Matsuda 55

A Novel Potential Way for Polyethylene Reuse: Reduction of NiO via Polyethylene Pyrolysis  
M. Cumbul Altay, S. Eroğlu 58

Comparison of Ozonation, Adsorption and Air Stripping Process for Ammonia Nitrogen Removal From Real Textile Wastewater  
Y. Gunes, F. Barut, G. Kaykioglu 60

Madder Root as an Adsorbent for Chemical Oxygen Demand, Color and Aromaticity Removal of Natural and Synthetic Dyeing Effluents  
E. Güneş, D.Çifçi, R. Atav, Y. Güneş 62

Green Synthesis of Pd/Fe Bimetallic Nanoparticles: Catalytic in situ Generation of H2O2 for Heterogeneous Fenton-like Decolourisation of Basic Red 46 and Direct Red 23  
M. Ergütt, A. Özer 64


Phosphorus removal from sludge centrant liquor by a packed-bed electrocoagulation reactor using iron scrap anodes  
S.M. Sarabi, P.I. Omwene, M. Kobya 68

Phosphorus Release and Nutrient Recovery from Waste Activated Sludge Through Mesophilic Alkaline Fermentation  
S. Cosgun, B. Kurt, N. Semerci 70

Preparation and Characterization of PDMS/SiO2 Mixed Matrix Membranes for Separation of Bio-alcohols from Fermentation Broths  
B. Demet, Y. Salt, C. Denktas, B. Özkaya 72

Nitrogen and Phosphorus Recovery from the Liquid Fraction of Anaerobic Digestate  
J. Al-Mallahi, R. O. Sürmeli, M. Çakiroğuz and B. Çalli 74

Potential Permeable Reactive Barrier Materials for the Treatment of Landfill Leachate  
E. B. Özkaraova, E. Güven Oral 76
Preliminary Results for Start-up and Adaptation of an EGSB Reactor for Valorization and Treatment of Source Separated Human Urine
M. N. Taher, M. Altinbas, B. Beler-Baykal 78

Electrodialysis Membrane Fouling, Scaling and Poisonning a Review and a Genereral Approach
K-E. Bouhidel 80

Boron Removal From Industrial Wastewaters by Means of Optimized Sequential Chemical Precipitation and Coagulation Processes
B. Özyurt, Ş. Camcıoğlu, M. Fırtın, Ç. Ateş, H. Hapoğlu 82

Evaluation of Electro-Fenton Method on Cheese Whey Treatment: Optimization Through Resonse Surface Methodology
Ş. Camcıoğlu, B. Özyurt, S. Şengül, H. Hapoğlu 84

Optimization of Combined Electrocoagulation/Electro-oxidation Process for Treatment of Sunflower Oil Industry Wastewater
Ş. Camcıoğlu, B. Özyurt, T. Sargıll, H. Hapoğlu 87

Innovative MEA Fabrication for Proton Exchange Membrane Water Electrolysis.
J.-W. Yu, G.-B. Ching, C.-C. Yeh, M.-Y. Kan, C.-Y. Lee, C.-J. Lai 90

A Numerical Comparison of Hydrogen Absorption/Desorption Behaviors of Uranium Based Metal Hydride Vessels (MHVs)
S. Yun, G. Gwak, H. Ju 92

Platinum Nanoparticles Recycling from Fuel Cells With Ionic Liquids

Optimization of Hardness Removal With Response Surface Methodology from Boron Containing Wastewater Using Bigadic Clinoptilolite
E. Calgan, E. Ozmetin, 96

The Pyrolysis Bioprocess Characterization and Thermogravimetric Analysis of Waste Corn
M. Sogancioglu, B. Karaagac, V. Sarialtin 98

Use of Polymer-Zeolite Based Composite Adsorbent for the Removal of Mixed Heavy Metals
M. Yıldız, Ç. Kivilçimdan Moral 101

Use of Ecotoxicology Tools Within the Environmental Footprint Evaluation Protocols: The Case of Wastewater Treatment Plants
R. Pedrazzani, E. Ziliani, I. Cavallotti, E. Bollati, M. Ferreri G. Bertanza 103

Environmental Burdens of Cataphoresis Process
P. N. Karaçal, N. Elginoz, F. Germirli Babuna 105

Olive Pomace Pyrolysis After Chemical Preprocessing
G. Dinc, E. Yel 106

Utilization of Sulfonated Polystyrene in the Treatment of Waste PS Plastic Washing Wastewater
N.C. Ozdemir, S.Safi, M. Soğancıoğlu, E. Yel 108

Thermoplastic Wastes Pyrolysis Char in the Epoxy Composite as Filler
E.Yel, M.Sogancioglu, G.Ahmetli 111

Evaluation of Nutrient Removal and Recovery by Electrochemical Process from Human Urine
E. Oztekin, H. İnan 114

Evaluation of Energy Recovery Potential of a Small Water Distribution Network using a Pump as Turbine System: Antalya-Kaleici Case Study
B. Seker, A. Muhammetoglu, H. Muhammetoglu 116

The Impact of Supplying Information and Awareness Raising on Public Attitude for Acceptance of Grey Water Reuse in Istanbul
J. Awayes, S. Cavkas, M. N. Taher, B. Beler-Baykal 119

Baseline Values of Greenhouse Gas Emissions for an Airport
S. Aksit Sahinkaya, F. Germirli Babuna 121

Assessment of Energy Efficiency in Wastewater Treatment
N. Semerci, B. Çalı 122

Which Effluent Quality for Which Reuse in the Mediterranean Region?
Burak, S. Ulker, D. 124
Influences of Microwave, MW/H\textsubscript{2}O\textsubscript{2} and MW/S\textsubscript{2}O\textsubscript{8} Pre-treatments on the BMP Potential of the Wastewater Sludges
E. Özön, A. Erdinçler

Electro-Fenton treatment of Nahtol Blue Black dye by using synthesized Dawson-type heteropolyanions as catalyst
A. G. Karaoglu, B. Ouahiba, N. Oturan, M. A. Oturan

Removal of Micropollutants by Membrane Distillation Bioreactor
A. Turan, M. Ince, Y.A. Uslu, E. Ince, E. Yükse, N. Ağbulut

Wastewater Treatment in Anoxic/Oxic-Membrane Bioreactor (A\textsubscript{2}O-MBR) by Assisted Ionizing Radiation
N. Ağbulut, E. Ince, Ö. Kantoğlu, M. Ince, E. Ergun, Y.A. Uslu, A. Turan, Ö. Kırkayak

Comparison of Aspen Modeling System Results to Performed Gasification Experiments
N. Karabağ, A. Öngen

Development of a Model of Biomass Gasification by Aspen Plus
N. Karabağ, S.S. Seyitoğlu, A. Öngen

Scaling and Biofouling as Limiting Factors for Membrane Treatment of Wastewater
M. Martienssen

Treatment of Microplastics
G. Kurtoglu Akkaya

Synthesis of NiFe LDH Deposited on Reduced Graphene Oxide for Degradation of Moxifloxacin by Sono-Photocatalytic Process
A. Khataee, S. Nikzat, T. Sadeghi Rad, M. Kobya

Fate and Distribution of Heavy Metals During Air-oxidant Gasification Processing of Treatment Plant Sludges
Azize Ayol and Özgün Tezer Yurdakoş

Chemical and Thermal Characteristics of Petro-Chemical Industrial Sludge
Özgün Tezer Yurdakoş and Azize Ayol

Inhibition Effect of Different TiO\textsubscript{2} Nanoparticles on the Oxygen Uptake Rate (OUR) of Activated Sludge Microorganisms
F. Çiner, R. Çalışan, B. Yüzer, H. Selçuk

Recycling Possibility of the Antioxidants in Olive Mill Wastewater by an Integrated Process
G. Çelik, I. Akmeht vendors Balçoğlu

Towards Sustainable Agricultural Waste Management: Reuse and Energy Recovery Potentials for Turkey
B. A. Alagöz, A. Erdinçler, O. Yenigün

Comparative Evaluation of Biogas Recovery During Anaerobic Treatment of Aircraft Deicing Fluids at Increased Ratios in Domestic Wastewater
H. M. Goktas, G. Engiz, E. Su, C. Yangin-Gomec

Comparative Efficiency and Environmental Impact Assessments of a Solar-Assisted Combined Cycle with Various Fuels Options
A. Karapekmez, I. Dincer

Water Clarification: Molecular Dynamics Simulation of Kaolinite-Water Interface in Saltwater for a Range of pH Values
G. R. Quezada, R. E. Rozas, P. G. Toledo

Micropollutant Removal from a Secondary Treated Municipal Wastewater by Electrodialysis

Decreasing Toxicity and Increasing Biodegradability of Dye Production Industrial Wastewater by Pre-Ozonation and Fenton Oxidation; Cost-Benefit Analysis of Wastewater Reuse System in Circular Economy Perspective

Decolorization and Detoxification of Textile Wastewater by Innovative and Cost Effective Ion-Exchange Process
A. T. Rapti, I. Aydin, B. Yuzer, H. Selcuk
Replacing Chloride in Textile Dyeing and the Synergistic Effects on a Hybrid Wastewater Treatment System  
M. I. Aydin, A. E. Ateş, B. Yuzer, Y. Oktem, H. E. Okten, H. Selcuk  

Use of Nano Zero-Valent Iron Coated Coffee Grounds Composite for Removal of Zinc and Nickel from Model Electroplating Waste Water  
A. Y. Goren, M. Genisoglu, A. Sofoğlu, H. E. Okten  

Life Cycle Assessment of Hydrogen-based Electricity Generation in place of Conventional Fuels for Residential Buildings  
M. Ozturk, I. Dincer  

Estimation of the air pollutants exposure and GHG emissions from the road transport in an urban area  
B. Onat, Ü. A. Şahin, B. Uzun, Ö. Akın, F. Özkaya, C. Ayvaz  

Reduction of VOC in Workplace Indoor Air With Ozone Application  
C. Ayvaz, Ü. Alver Şahin, B. Onat, B. Uzun, Y. Dumanoğlu  

Composting of Sludge by Soil Worms and Monitoring of Vermicompost Quality  
F. Ekmekyapar, S. Akyurt  

Development of a New Integrated Textile Wastewater Treatment and Hydrogen Production System with Ion Exchange Membranes  
B. Yuzer, H. Selcuk, I. Dincer  

Economic Analysis and Design of A Hybrid Autonomous Floating Photovoltaic-Fuel Cell System integrated with A Hydrogen Production Unit  
M. Temiz, N. Javani  

Assessment of Net Additions to Stock and Embodied Energy for Eryaman District, Turkey via 3D GIS  
N. Reçber, H. Şengül  

POSTER PRESENTATIONS  

Determination of Transport Coefficients of Inorganic Contaminants Through Alternative Liner Systems from Leachate to Groundwater Using One-Dimensional Mass Transport Model  
G. Varank, A. Adiller, S. Y. Guvenc, A. Demir, E. Adar  

Treatment of Tannery Industry Wastewater by Electrocoagulation Process Using Iron Electrodes  
S. Y. Guvenc, G. Varank  

Degradation of the Endocrine Disrupting Micropollutant Bisphenol A with Persulfate - and Peroxymonsulfate-enhanced Ozonation Processes  
I. Arslan-Alaton, T. Olmez-Hanci, R. Sert  

Leachate Treatment by Electrocoagulation Methods  
Ö. Apaydın, E. Özkan  

Adsorption of Ketoprofen onto powdered activated carbon: Effect of adsorbent dose and solution temperature  
M. Zamouche, A. Ayachi, I. Merniz  

High Performance Adsorption Capability of Geopolymer Prepared from Tin Tailing Minerals  
Is Fatimah, Putwi Widya Citradewi, Khoirunnisa  

Physicochemical and Photocatalytic Studies of ZnO-supported Indonesian Kaolinite (ZnO/Kaolinite) for Methyl Violet Photo-oxidation  
E. Desiyani, F. Harjati, I. Fatimah  

Preparation of Activated Carbon from Waste Tire and Its Use for Dye Remove  
E. Elmaslar Özbaş, B. Balçık, H.K. Özcan  

Degradation of Olive Pomace by Thermochemical Methods  
E. Elmaslar Özbaş, H.K. Özcan, A. Öngen,  

Change in the Avaliable and Toxic Concentrations of Metals in the Soil When Compost and Commercial Soil Conditioners are Used  
E. Elmaslar Özbaş, A. Çatalbaş  

Effect of The Thermal Processes Solid Product on Plant Growth for “Allium Ascalonicum”  
E. Elmaslar Özbaş, A. Öngen, H.K. Özcan, B. Keleş, E. Topuz  

The Effects of Thermal Prosses Solid Product on Development of Cicar Arietinum L.  
E. Elmaslar Özbaş, A. Öngen, H.K. Özcan, E. Adıgüzel, E. Mavzer
Recycling of Wastewater from Petroleum Refinery  
E. Elmaslar Özbaş, H.K. Özcan, A. Öngen, S. Aydin, S. Güneysu, E. Mert 232

Reuse of Waste Water for Agricultural Irrigation  
E. Elmaslar Özbaş, H.K. Özcan, A. Öngen, S. Aydin, S. Güneysu, N. Kulak 234

Investigation of Energy Recovery from Waste Paper Cups  
H. K. Özcan, A. Öngen, S. Yigit Hunce, E. E. Ozbas, S. Aydin, G. Korkmaz, B. Başlı 236

Photo Fenton-like Degradation of Methylene Blue with Cobalt Ferrite Nanoparticles  
P. Karacabey, M. Ergütt, D. Uzunoğlu, A. Özer 238

Colorimetric Detection of Fe$^{3+}$ Ions in Aqueous Solution Using Green-Synthesized Silver Nanoparticles  
C. G. Koduman, M. Ergütt, D. Uzunoğlu, A. Özer 240

Removal of Reactive Black 5 With Fenton Oxidation From Aqueous Solutions And Optimization of Response Surface Methodology  
Y. Süzen, C. Özmetin 242

D-optimal Design Study of Reactive Extraction of Propionic Acid with Imidazolium-Based Ionic Liquids  
N. Baylan 244

Separation of Valeric Acid from Aqueous Solutions by Reactive Extraction using 1-Hexyl-3-methylimidazolium hexafluorophosphate  
N. Baylan 246

Lactic Acid Recovery from Water by Amberlite IRA-400  
N. Halilıbrahimoğlu, İ. İnci, N. Baylan 248

Removal of Ciprofloxacin Hydrochloride from Water by Adsorption with Various Adsorbents  
A. Avci, İ. İnci, N. Baylan 250

Comparison of Centralized and Source Separation System for Sustainability  
Z. Çetinkaya Ateşiç, H. İnan 252

Efforts to promote the recovery of hydrogen gas from municipal solid waste incineration bottom ash (MSWIBA) by using catalysts  
M. Miyake, A. Saffarzadeh, T. Komiya, T. Shimaoka 254

Adsorption of cationic methylene Blue (MB) dye onto natural untreated clay (NUC) : Kinetics, equilibrium and thermodynamics  
S. Dadou, T. Berrama, C. Zekkaoui, S. Benredouane, A. Beriber 256

Optimization of the emerging pollutant elimination by adsorption process: Application of Doehlert design  
C. Zekkaoui, T. Berrama, S. Dadou, N. Doufene, S. Benredouane 260

Process Parameters Optimization of Graphite-Graphite Electro-Fenton System for the Treatment of Sunflower Oil Refining Industry Wastewater  
B. Özyurt, Ş. Camcıoğlu, M. Fırtın, H. Hapoğlu 262

Epoxy Composites with Washed PS Wastes’ Pyrolysis Char Additives  
M. Sogancioğlu, E. Yel, G. Ahmetli 264

Removing of Micro-plastics and Surfactant from Domestic Laundry Wastewaters  
F. Deveci, H. İnan 266

Insights into nonlinear adsorption kinetics and isotherms of vanadium using magnetized coal-polyaniline  
G. W. Kajumba, F. Osra, S. Aydin, S. Emik, E. Yıldırım 269

Deinking of Waste Office Paper by Chemical Flotation in Recycling  
M. Celebi, E. Yel 272

Membrane Distillation Bioreactors  
Y. A. Uslu, M. İnce, A. Turan, E. İnce, N. Ağbulut 274

Ceria based electrolyte materials co-doped with rare-earth elements for Solid Oxide Fuel Cell  
A. Arabacı 277

The Effects of Green Roof Application on Urban Life for Water and Energy  
A. Koca, H. İnan 279

Enzyme Activity Test and Antimicrobial Activity From Fermentation of Pineapple Fruit (Ananas comosus Merr.)  
H. Hidayat, V. Amanda 281
Comparing the European Union and Turkey Plastic Recycling Strategy
B.B. Palabıyık, Y.A. Oktem

A Study on Numerical Simulation of Contaminated Site Capping
M. Balkaya

Microplastics in Sediments of the Golden Horn Estuary (Halic), Istanbul, Turkey
P. Dogruyol, M. Sener, N. Balkaya

Assessment of the Geotechnical Aspect of the Use of Paper Mill Sludge as Landfill Cover Material
M. Balkaya

Microplastic Pollution in the Blacksea Coast of Istanbul, Turkey
M. Sener, P. Dogruyol, N. Balkaya

Evaluation of the Usage of Various Capping Materials in In-Situ Capping of Contaminated Sediments
M. Balkaya

Assessment of Heavy Metal Contamination in Urban Soil (Tuzla District, Istanbul, Turkey)
N. Sezgin, N. Balkaya, A. Sahmurova, N. Aysal

Evaluation of Safe Closure Process Alternatives for Submarine Tailings Disposal Pipelines of Mines
S. Nemlioglu, N. Sezgin, U.E. Temelli

Reuse of Domestic Wastewater Marine Outfall after Hybrid Port Change Rehabilitation Alternatives of Diffusers with Duckbill Check Valves
S. Nemlioglu, C. B. Cobanoglu Kayikci

Multivariate Statistical Analysis of Trace Metals in Istanbul Road Dust
N. Sezgin

Biodiesel Production From Microalgae in Wastewater
A.E. Ateş, S. Ateş

A Study on the Impact of Noise on Anger in Young Adults
A. Sahmurova, N. Balkaya, G. Alpar, P. Sezgin

Phosphate Removal from Wastewater by using Water Treatment Sludge
N. Balkaya, E. Erkan

Removal of Methylene Blue by Cationic Resin and Regeneration Studies
S. Gunes, O. Al., R. Boncuakcuoglu

The Use of Sensors for Monitoring Particulate Matters in Urban Air of Istanbul
Ü. Alver Şahin, C. Ayvaz, B. Onat, B. Uzun, İ. Çelikkol, M. Efe, M. Doğan

Determination of Volatile Organic Compounds in an Adhesive Tape Production Factory Workplace Air.
Ü. Alver Şahin, B. Onat, N.E. İlkılıç, B. Uzun, C. Ayvaz, Y. Dumanoğlu, Ö. Akin

Cadmium Removal Using Potato Peels as Adsorbent; Kinetic Studies
B.B. Palabıyık, H. Selçuk, Y.A. Oktem

Authors Index

Sponsors

xiii
ORAL PRESENTATIONS
Utilization of Lime, Gypsum and Cement as an Additive Material in Liner System

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Keywords: Kaolinite, Consistency Limits, salt solution, lime, gypsum, cement

Abstract

In this study effect of NaCl, an inorganic salt solution on consistency limits of kaolinite and kaolinite mixtures was investigated. Since the use of distilled water or tap water is far from being representative for leachate, NaCl salt solutions at different molarities were used in the experimental study to define the geotechnical characteristics of kaolinite and kaolinite mixtures as liner materials. Lime, gypsum and Cement were added in percentages of 5 and 10%, by dry weight of the kaolinite. Results of the study showed that the liquid limit decreases, plastic limit increases and plasticity index decreases with increasing chemical concentration for high plasticity clay therefore in a broad approach it can be concluded that the hydraulic conductivity increases with increasing chemical concentration for high plasticity clay. Moreover increase in plastic limit and decrease in likit limit and plasticity index of the kaolinite mixtures was found to be lower. Improvement in geotechnical properties of kaolite and kaolinite mixtures was also observed at utilization of the additives.

1. Introduction

The liner system is one of the most important elements of a modern engineered landfill. Compacted clay liners are the main components of composite liner systems consisting of a geomembrane overlaying a compacted soil liner or a geosynthetic clay liner. The clays are exposed to various chemical, biological and physical reactions occurring in the landfill body and affected by the resulting leachate. It is well known that the mechanical and hydraulic behaviour of clay soils can be strongly affected by the clay–leachate interaction (Yılmaz et al., 2008).

In recent years, many researches have been focused on the interaction of clay soils with different types of fluids to determine the effect of landfill leachate on geotechnical properties of liner materials especially on hydraulic conductivity (Schmitz et al., 2004; Jo et al., 2005; Park et al., 2006; Abdi et al., 2008; Yılmaz et al., 2008; Shariatmadari et al., 2011). Hydraulic conductivity is the key parameter for barrier soils in contaminant migration from leachate to groundwater one of the important basic soil characteristics. Since the determination of hydraulic conductivity values of soils takes a long time, the effect of fluid on hydraulic conductivity of the barrier soil can be estimated by the consistency limit tests (Schmitz et al., 2004).

Atterberg limits could be used as a representative parameter to estimate clay behavior and could be correlated with various engineering properties such as permeability, shrinking and swelling behavior, shear strength, and compressibility of the soil (Shariatmadari et al., 2011; Arasan and Yetimoglu, 2008). Evaluation of the consistency limits provides some very basic
mechanical data about the soil and also gives a first insight into the chemical reactivity of clays. Additionally some additive materials can be used to improve the geotechnical properties of clay liners for interaction with fluid. The additive materials can limit the change in consistency limits before and after being exposed to the fluid.

The present study was undertaken to investigate the effect of salt solution on consistency limits of kaolinite and kaolinite mixtures obtained by using lime, gypsum and cement as additive materials.

2. Materials and Methods

Liner materials were classified according to Unified Soil Classification System (USCS) (ASTM D 2487) and index parameters of the liner materials were determined by Atterberg tests (ASTM D 4318). The experimental work included the addition of different percentages of lime, gypsum and cement (5 and 10% of dry weight of soil) to the kaolinite. NaCl salt solutions were used in different normalities (0.01, 0.1 and 1 N)

3. Results and Discussion

Kaolinite can be classified as CH-Class (LL>50) high plasticity clay according to the Unified Soil Classification System (USCS).

3.1. XRD graph

XRD graph of the kaolinite is given in Figure 1. Clay consists of quartz, kaolinit ve alunit components

![XRD graph of kaolinite](image)

Figure 1. XRD graph of kaolinite

References


Do we really need to remove trace pollutants from wastewater? An innovative assessment approach

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Keywords: decision support, environmental toxicity, human toxicity, impact categories, tertiary treatment

Abstract

Trace pollutant detection and removal has been considered a critical issue since the first works published in the international literature revealed their presence in wastewater and wastewater treatment plant effluents. A lot of efforts are being done in several directions: 1) detection of numerous substances in water, wastewater, sludge and environmental matrixes; 2) environmental and human toxicity assessment; 3) removal of trace pollutants from wastewater; 4) study of alternative compounds to be used instead of the harmful ones. In the meanwhile, some plants have been equipped with tertiary treatment stage addressed to the removal of trace pollutants. Now the question is: is it the right choice?

1. Introduction

Trace pollutants discharge into the environment is considered a serious issue to be faced. Monitoring of priority substances in the water bodies is requested by European directives (60/2000 and subsequent updating). Wastewater treatment plant (WWTP) effluents are recognized as a major source. Several treatment technologies have been proposed for removing these substances from wastewater; among them, well established processes (such as activated carbon and advanced oxidation) showed their capacity to reduce residual concentrations below detection limits. This at least is what emerges when the target compounds are measured. Nevertheless, intermediate compounds are also generated as by-products, their nature and concentration depending on many uncontrollable variables (wastewater characteristics, process conditions, etc.). It has been observed that by-products may be even more toxic than the parent compounds. Moreover, adding treatment stages to a conventional WWTP for removing trace pollutants (and hopefully improving the effluent quality) means also increasing chemicals and/or energy consumption. This, eventually leads to a secondary impact on the environment (and human health), for example related to increased gaseous emissions.

The evaluation of what is the best solution to adopt is then very complex: several aspects have to be considered simultaneously and assessment tools must be developed and standardised.

2. Materials and Methods

The work presented here concerns three research areas, which are involved in the attempt of answering the question in the title, through the development of:
1. bioassays which are able to directly measure the combined effect of unknown pollutants in water and sludge;

2. models for comparing the environmental impact on different environmental domains (e.g. water bodies vs atmosphere) and/or methods for using results of bioassays in standardized Life Cycle Assessment (LCA) protocols;

3. procedures for an integrated assessment of different options, based on a multicriteria approach: several aspects must be simultaneously accounted for, related to technical, environmental, economic issues.

As for the first point, results of recent studies (Bertanza et al., 2011; Papa et al., 2016a; Gonzalez-Gil et al., 2016) and on-going research activity are presented. The use of bioassays for the characterisation of wastewater and sludge is presented, in order to show the potential of this approach.

The evaluation of the environmental impact of treatment technologies is discussed by showing the results of works based either on innovative modelling approach (Papa et al., 2016b) or on a non conventional use of the LCA methods (Pedrazzani et al., 2018).

Finally, the integrated assessment and decision making process is analysed by presenting some case studies where an easy-to-use procedure has been developed and applied (Bertanza et al., 2017; Bertanza et al., 2018).

The examples presented in this work show the complexity of this problem and also underline that only an integrated and multidisciplinary approach can put on the right way for trying to find suitable solutions. Unfortunately, there is still much work to do.

References


Release of Metals and Nutrients during Sewage Sludge Hydrolysis by Rhamnolipid and Saponin

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Keywords: biosurfactant, hydrolysis, industrial sludge, municipal sludge, rhamnolipid, saponin.

Abstract

This study investigated the effects of two types of biosurfactants (rhamnolipid and saponin) on sewage sludge hydrolysis. A hydrolysis process with rhamnolipid and saponin was evaluated for releasing metals and nutrients from municipal sludge and industrial sludge. Concentration of biosurfactant and biosurfactant/sludge ratio was optimized. Release of metals, heavy metals, nitrogen and phosphorus were analyzed. The release of Fe, Zn and Cr from industrial sludge using rhamnolipid was much higher when rhamnolipid/sludge ratio was 5/1 in 7% rhamnolipid solution. A significant amount of nitrogen and phosphorus release from municipal sludge was observed by using rhamnolipid and saponin.

1. Introduction

Over the past few decades, many approaches for the sludge treatment and disposal have been introduced. These methods include chemical treatments, ion exchange methods, thermal treatments, bioleaching methods, electrokinetics methods, ultrasound-assisted nitric acid methods. Especially, the chemical methods have been focused more than others methods by researcher, due to its simple operation processes, the short operation times, and high removal efficiency for heavy metals in the sludge. Various organic acids, inorganic acids and chelating agent have been applied to remove heavy metals from the sludge efficiently (Tang et al., 2017). However, a large of chemical reagent dosages and low pH can obtain high removal efficiency, which results in high processing costs and difficulty in pH adjustment of the treatment sludge. Therefore, it is necessary to find environmental friendly reagents take the place of the organic acids, inorganic acids and chelating agents (Tang et al., 2017). Biosurfactants are bioavailable surface-active compounds mainly produced by bacteria, fungi and yeasts (Ozturk et al., 2012). Also, biosurfactants can also be extracted from the metabolites of plants. Biosurfactants can form micelles and reduce surface and interfacial tension. Consequently, biosurfactants can effectively solubilize, disperse and desorb both organic and heavy metals (Gao et al., 2012). Also, biosurfactants can change the morphology of sludge flocs (Yi et al., 2013). The applications of different types of biosurfactants in the release of metals and nutrients from municipal sludge and industrial sludge have rarely been studied. In this study, we compared the effects of two types of biosurfactants (saponin and rhamnolipid) on sludge hydrolysis. The release of metals, heavy metals, nitrogen and phosphorus was quantified.

2. Materials and Methods

Digested municipal sludge was obtained from an anaerobic digester effluent in a sewage treatment plant in Antalya, Turkey. Thickened industrial sludge was provided from an organized industry region wastewater treatment plant located in Isparta, Turkey. The
sludge samples were oven dried at 103±2 °C for 42 h, then finely grounded and sieved to 1 mm mesh size. Rhamnolipid containing 90% of pure rhamnolipid was purchased from AGAE Technologies (USA). Saponin from quillaja bark was purchased from Sigma-Aldrich. The maximum sapogenin content was 30%. Hydrolysis was performed in a batch tests using magnetic stirrer for 4 h. Blank tests were conducted without rhamnolipid, in parallel.

3. Results

This study focused on the investigation of hydrolysis of municipal sludge and industrial sludge using by biosurfactant. Compared to the blank tests, the release of Fe, Zn and Cr from industrial sludge using rhamnolipid were much higher when rhamnolipid/sludge ratio was 5/1 in 7% rhamnolipid solution (Fig. 1). The highest releases of nitrogen and phosphorus from municipal sludge were obtained in in 10% rhamnolipid solution and 5/1 rhamnolipid/sludge ratio. The metals, nitrogen and phosphorus release concentrations generally increased with the decreased of the rhamnolipid/sludge ratio.

Acknowledgement

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References


Enhanced Solar-Driven Water Splitting of 1D Core-Shell Silicon-Metal Oxide Nanopillars

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Keywords: silicon pillars, ZnO, TiO2, solar water splitting, ALD.

Abstract

1D core-shell Si/metal oxide nanopillar (NP) photoanodes were synthesized for enhanced solar-driven water splitting processes. The core-shell structures were fabricated by atomic layer deposition of different metal oxides (e.g. ZnO, TiO2) onto Si nanopillars, which were synthesized by metal-assisted chemical etching and nanosphere lithography. In order to characterize produced photoanodes various experimental techniques (SEM/TEM, XRD, XPS, Raman spectroscopy etc.) were applied. Photoelectrochemical (PEC) water oxidation of produced photoanodes was studied. We showed that composition of n-Si/TiO2/ZnO NP exhibited enhanced photocurrents due to barrier effects. Optimal morphological and compositional parameter for enhanced PEC water splitting were found. The relationship between the PEC performance and the electrolyte pH was also discussed.

1. Introduction

Photoelectrochemical (PEC) water splitting is a direct route to capture solar irradiation and to produce hydrogen. One of the main challenges in PEC water splitting is the development of photoanodes with high stability and efficiency [1]. Among multidimensional nanostructures, 1D nanostructures (nanowires, nanopillars, nanotubes etc.) is considered to be more efficient among them. Nanostructured Si is commonly used for PEC water splitting due to its enhanced absorption properties and high surface area [2 –4]. However, Si photoelectrodes undergoes irreversible changes induced by corrosion and surface passivation during the electrochemical reactions. Therefore, a composite semiconductor electrode based on the heterojunction should be proposed to overcome these shortcomings. The use of TiO2 as a shell to protect Si from corrosion is straightforward because it is considered as one of the most stable photocatalytic materials [5 –8]. Because of its high Eg (~3 eV), TiO2 shell transmits visible light which can be further absorbed by Si core.

2. Materials and Methods

In this article, we report a fabrication of Si/TiO2 core-shell NP photoanodes by a combination of nanosphere lithography, metal-assisted chemical etching (MACE), and Atomic Layer Deposition (ALD). Characterization of working electrode was performed using the potentionstat-galvanostat system AutoLab PGStat 302N in a standard three-electrode assembly. The samples were irradiated with a 150 W Xenon lamp (Osram XBO 150) equipped with an AM 1.5 filter allowing to obtain simulated solar light. The irradiance of incident light was calibrated to 100 mW/cm².
3. Results

The Si/metal oxide (Si/TiO₂, Si/ZnO, Si/TiO₂/ZnO and Si/ZnO/TiO₂) core-shell NP photoanodes were fabricated via the effective and facile method based on a two-step route combining MACE and ALD. The morphology, optical and PEC properties of Si/ metal oxide core-shell NP photoanodes were studied. Developed photoanodes based on Si/TiO₂/ZnO composites exhibit enhanced photoactivity for water splitting due to the more effective photo-generated carriers, the carrier separation at the ZnO-TiO₂-Si interface and large specific surface area which increase the light capture (Fig.1). This work suggests that metal oxide ALD coating can bring significant performance gain to Si NP photoanodes in terms of both charge separation efficiency and catalyst stability. The results demonstrate the advantage of nanopillar core-shell heterostructures in photocatalytic water splitting processes.

![Figure 1](image)

**Figure 1.** Linear voltammetry curves of photocurrent density versus potential in Si/TiO₂/ZnO NP (left) and Photocurrent stability (right).

References


Elimination of Antibiotic Resistance at Urban Wastewater Treatment Plants by Iron-based Heterogeneous Advanced Oxidation Processes

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Keywords: Antibiotic resistance, urban wastewater, disinfection, iron-based advanced oxidation processes, multi-resistant E-coli J54 bacteria

Abstract

Due to the fact that effluents from sewage treatment works are a major source of antibiotic resistance, they create a serious risk to public health and in ecosystems (Ben et al., 2017). Our research group currently works on the implementation of novel, sustainable and at the same time advanced, high-performance treatment systems including iron-based advanced oxidation processes for the elimination of antibiotic resistant bacteria and their genetic materials. Within the scope of this research project, some heterogeneous iron-based advanced oxidation processes including zero-valent iron (Fe⁰) and goethite (α-FeOOH)-activated hydrogen peroxide will be applied to simulated urban wastewater containing the conjugative, multi-antibiotic resistance plasmid RK4 carrier multi-resistant E-coli J54 strain. Disinfection performance (removal of antibiotic resistance) will be compared with those of conventional disinfection processes (chlorination, ozonation and UV-C radiation). The inherent advantages of using iron-based advanced oxidation processes in eliminating not only antibiotic residues but also antibiotic resistance will be demonstrated.

1. Introduction

The unconscious use of antibiotics has led to serious health risks as well as environmental problems in aquatic and terrestrial environments. The so-called “super bacteria” which are extremely resistant to most wide-spectrum, commercially important antibiotics, originate from aquaculture, animal farms, agricultural activities as well as hospitals and household effluent (Ben et al., 2017; Ory et al., 2016). They are drained into the sewage treatment works where they are not effectively eliminated by conventional disinfection methods and hence re-enter the drinking water sources where they continue to harm the public health and environment (Xu et al., 2015; Ferro et al., 2016; Zanotto et al., 2016). In this way antibiotic resistant bacteria and their genetic materials are spreading quickly in all environmental compartments which situation renders their control and elimination a difficult task. Hence, their identification, control and elimination have attracted great attention in the recent past. Current disinfection technologies applied at water and wastewater treatment works, including ozonation, UV-C photolysis, chlorine, chlorine dioxide and hydrogen peroxide bleaching in the presence of sunlight, are not sufficient to eliminate antibiotic resistance (Ndounla et al., 2014; Oh et al., 2014). Obviously, it is important to treat antibiotic resistance as a challenging environmental pollution parameter by employing more advanced physicochemical treatment processes to effectively eliminate multi-resistant bacteria and genes (Guo et al., 2017; Li et al., 2015; Lin et al., 2012).
2. Materials and Methods

In the present study, owing to its conjugative multi-antibiotic resistance plasmid RK4, the ampicillin (Amp\textsuperscript{R}), kanamycin (Km\textsuperscript{R}) and tetracycline (Tc\textsuperscript{R}) multi-resistant \textit{E. coli} J53 strain and its \textit{bla} TEM-2 (ampicillin resistance gene), \textit{aphA} (kanamycin resistance gene) and \textit{tetA} (tetracycline resistance gene) antibiotic resistant genes located on the RK4 plasmid were selected as models to examine the elimination of antibiotic resistance from simulated urban wastewater (COD=150 mg/L; BOD\textsubscript{7}=100 mg/L; TOC=50 mg/L) by employing heterogeneous, iron-based advanced oxidation processes (zero-valent iron and goethite-activated hydrogen peroxide). For this purpose, synthetic urban wastewater samples will be prepared and thereafter contaminated with multi-antibiotic resistant \textit{E. coli} J53 cells. Beforehand, the selected advanced treatment processes will be optimized in terms of the operating variables pH (5,6,7), oxidant (hydrogen peroxide, 0.0-1.0 mM) and heterogeneous iron catalyst (Fe\textsuperscript{0} and \textit{α}-FeOOH, 1-5 g/L) concentrations. Their inactivation performance will be examined by following the number of alive, multi-resistant \textit{E. coli} cells as well as the gene copy numbers of the \textit{bla} TEM-2, \textit{aphA} ve \textit{tetA} -resistant genes before and after application of iron-based advanced oxidation processes. The inactivation performance of the iron-based advanced oxidation processes will be evaluated and compared with conventional disinfection processes (chlorination, ozonation and direct UV-C photolysis).

3. Results

Within the scope of this study it is expected to propose alternative treatment (disinfection, advanced oxidation) systems that can effectively cope with multi-antibiotic resistant bacteria and their genes present in the effluent of sewage treatment works. The control and elimination of antibiotic resistance as an environmental pollution parameter is an emerging concept and deserves special attention for the sake of public health and sustainable water resources management.

References

The Potential of Water Saving in Buildings: Greywater Reuse

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Keywords: Greywater, reuse, wastewater, wetland

Abstract

Greywater treatment and reuse is an alternative to provide non-potable water to households and reduce the water usage per person by up to 50%, or even more (Zavala et al., 2016). The aim of the study was to evaluate the water saving potential of buildings. A 5-story building was chosen as case study and the existed fixtures of this building were determined. Plan of the building is shown in Figure 1.

![Figure 1. Plan of the building](image)

The amount of total wastewater and greywater was calculated regarding to average accepted values. Wastewater produced from kitchen was not considered as greywater. It was assumed that 48 people are living in this building, considering 12 apartments in the building and four people live in each apartment. Total amount of wastewater and greywater was calculated as 9120 L/day and 5568 L/day, respectively. BOD5, SS, TN, and TP concentration of greywater was accepted as 125, 50, 10, and 4 mg/L, respectively.

To collect greywater separately, some infrastructure modifications are required. Therefore, new fixtures were designed for the separation of greywater from black water and the cost of
new fixture installation was determined as about 14,700 USD while the cost of the existing fixture implementation was calculated as 13,550 USD. It was assumed that separately collected greywater will be treated by a constructed wetland system. Greywater may include lint from washing machines, hair from baths and showers, and grit from several sources. They can clog pipes, pumps and treatment systems; therefore, a pre-treatment is needed. The treatment system was consisted of a two-way valve, a coarse filter, an equalization tank, a vegetated submerged bed wetland, and UV disinfection (Figure 2). The wetland system was designed considering the methods given by EPA (USEPA, 2000) and the required surface area of the wetland was calculated as 120 m². Disinfection by UV was selected to eliminate possible pathogens from greywater.

Figure 2. Greywater fixtures and treatment systems

It was assumed that treated greywater is pumped to the 5-m³ storage tank and it is used for toilet flushing and irrigation of garden. As a result, water saving potential of this building, and the investment and operational cost of the reuse of greywater were calculated. Based on these data, the amortization period of additional investments was determined.

This paper is directly related with the conference topics of “Wastewater treatment, recycling and reuse technologies”. The results include the practical application of theory and they will be interesting and helpful for participants.

References
Effect of Phosphate on Anammox Process

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Keywords: Anammox, inhibition, phosphate, nitrogen removal rate, sludge digester effluent

Abstract

Anaerobic ammonium oxidation (Anammox), an innovative technological process used for the treatment of nitrogen-rich wastewater streams. However, the Anammox process is inhibited by many compounds, such as substrates (ammonia and nitrite), organic matter, salt, heavy metals and sulfide. There are also few numbers of publications in which phosphate is stated to be inhibitory for Anammox bacteria. However, there are some inconsistencies in the inhibition threshold values presented. Therefore, in this study, the effects of phosphate on Anammox process in treating ammonium rich and phosphate containing sludge digester effluent taken from a full-scale municipal WWTP, in Istanbul, Turkey was investigated. The phosphate level in the influent of the laboratory scale upflow packed bed anammox (UPBAn) reactor gradually increased from 26 to 541 mg PO₄/L. As a result, no adverse effect on the nitrogen removal performance was observed during 281-day operation. The nitrogen removal rate (NRR) of 0.35 kg N/m³/d was observed when phosphate was 67 mg/L whereas NRR was increased to 0.99 kg N/m³/d in the presence of 541 mg PO₄/L.

1. Introduction

Conventionally, treatment of ammonium with the consumption of organic matter as carbon source can be achieved by nitrification followed by a denitrification process. Anaerobic ammonium oxidation (anammox) process is an alternative innovative process which was firstly discovered in 1995 in a denitrifying fluidized bed reactor (Mulder et al., 1995). Anammox bacteria are capable of converting ammonia under anaerobic conditions with nitrite into N₂ gas. It can reduce aeration by 64%, exogenous electron donors by 100%, and sludge production by 80-90% (Chen et al., 2016). However, the application of the Anammox process is restricted by some inhibition compounds existing in nitrogen-rich wastewater. In the present study, ammonium treatment of a side stream effluent which is returned to the main water line in a full scale wastewater treatment plant was investigated in a laboratory scale experiment by two stage partial nitritation-anammox process for treatment of anaerobic sludge digester effluent. The objective of this study is to evaluate the effect of phosphate concentration on Anammox process.

2. Materials and Methods

The anaerobic ammonium oxidation experiment was performed in a 4.8-L glass upflow reactor filled with packing materials. The upflow packed bed anammox (UPBAn) reactor was inoculated with 1 L of activated sludge taken from the sludge recycling line of Paşaköy...
WWTP, in Istanbul, Turkey. The reactor was fed with the centrate of sludge digester effluent of Istanbul-Ambarlı WWTP as summarized in Table 1.

**Table 1.** The characteristics of sludge digester effluent used in the study

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sCOD (mg/L)</td>
<td>236±59.2</td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>83±13.2</td>
</tr>
<tr>
<td>NH₄⁺-N (mg/L)</td>
<td>551±108</td>
</tr>
<tr>
<td>PO₄ (mg/L)</td>
<td>428±113</td>
</tr>
<tr>
<td>Total Suspended solids (mg/L)</td>
<td>193±86</td>
</tr>
<tr>
<td>Volatile Suspended solids (mg/L)</td>
<td>122±47.3</td>
</tr>
<tr>
<td>pH</td>
<td>7.50±0.14</td>
</tr>
<tr>
<td>Conductivity (µs/cm)</td>
<td>5710±1708</td>
</tr>
<tr>
<td>Alkalinity (mg/L)</td>
<td>1982±347</td>
</tr>
</tbody>
</table>

Sample number=130

3. Results

The phosphate level in the influent of the laboratory scale upflow packed bed anammox (UPBAn) reactor gradually increased from 26 to 541 mg PO₄/L throughout 281-day operation. The nitrogen removal rate (NRR) of 0.35 kg N/m³/d was observed when phosphate was 67 mg/L whereas in the presence of 541 mg PO₄/L, NRR was increased to 0.99 kg N/m³/d. Based on these results, in contrast to some former studies, it was determined that phosphate has exerted no inhibitory effect on Anammox process up to 550 mg/l (Jin et al., 2012; Zhang et al., 2017).

![Figure 1. Profiles of Nitrogen Removal Rate (NRR) and PO₄ concentration in the Anammox reactor.](image_url)

**References**


Evaluation of Municipal and Petrochemical Industry Sludges as a Feedstock for Biodiesel Production: Effect of the Acid and Combined Acid/Microwave Pre-treatments

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Keywords: biodiesel, lipid, municipal sludge, petrochemical sludge, liquid-liquid extraction

Abstract

Municipal and petrochemical industry wastewater sludges have high lipid content and can be used as feedstocks for biodiesel production. The first step in biodiesel production is the extraction of lipids. Most of the lipid extraction methods involve sludge drying step. The novel direct liquid-liquid lipid extraction method, makes it possible to use the sludge directly in liquid form, eliminating the expensive drying step. The aim of this study was to explore lipid extraction and biodiesel production yields from municipal and petrochemical industry wastewater treatment plant (WWTP) sludges by using the direct liquid-liquid lipid extraction method. The study also investigated the effect of acid and combined acid/microwave pre-treatments on the lipid and biodiesel yields of the sludge samples. The results of the study showed that acid and combined acid/microwave pre-treatments increased the lipid and biodiesel yields. The highest lipid yield was obtained by application of combined acid/microwave pre-treatment to the petrochemical industry WWTP sludge.

1. Introduction

Energy has become an important factor for industrial and economic development. Nowadays, 81% of world energy production is coming from fossil fuel sources (IEA, 2017), but there are economical and environmental problems with their utilization. For these reasons, biodiesel is emerging as a great alternative fuel because of its renewable nature and environmental benefits (Ferella et al., 2010). There are different feedstocks for biodiesel production such as edible and non-edible plant oils, animal fats, waste cooking oil, microalgae and the wastewater sludges. Among the these alternative sources, wastewater sludge is gaining importance around the world because of its advantages over conventional diesel. The volume of wastewater sludges generated by domestic and industrial sources has increased with the urbanisation and economic development. The municipal primary sludge is a mixture of floating grease and solids, mainly simple organic compounds, collected at the bottom of the primary settler. On the other hand, the petrochemical industry sludge taken from the thickening unit of wastewater treatment plant (WWTP), contains sludges from oil separators, primary clarifier, and the waste activated sludge from the secondary clarifier. It also comprises of various organic and inorganic compounds. In literature, dried sludge has been used directly as a raw material for lipid extraction. As wastewater sludge has higher water content of 95-98% wt, the energy cost of dewatering and drying processes constitutes almost 50% of the total biodiesel production cost, making the process very expensive and
difficult to scale up (Olkiewicz et al., 2012). A novel direct liquid-liquid lipid extraction method introduced by Olkiewicz et al. (2014), eliminates the sludge drying and dewatering steps by using the sludge samples in the liquid form and makes the process effective in terms of energy and cost.

2. Materials and Methods

In the study, the municipal wastewater sludge samples were collected at the bottom of the primary clarifier of a municipal wastewater treatment plant located in Istanbul; whereas the oily sludge samples were obtained from thickening unit of a petrochemical industry wastewater treatment plant (WWTP) in Turkey.

Sludge samples were acid pretreated by using hydrochloric acid (1N HCl) to decrease their pH to 2 before the lipid extraction process. In the combined acid/microwave pretreatment, the acidified sludge samples were microwave irradiated by using a Berghof Microwave System (MWS+3). Liquid–liquid extraction of lipids was performed by using a mixing and settling batch reactor set to understand its feasibility. The lipids were converted into fatty acid methyl esters (FAMEs/biodiesel) through the acid catalyzed transesterification process.

3. Results

The petrochemical industry WWTP sludge having higher lipid content than the municipal wastewater sludge is found to be a more appropriate feedstock for biodiesel production. The acid and combined acid/microwave pre-treatments improved the lipid and biodiesel yields obtained from both of municipal and petrochemical industry WWTP sludges. The application of combined acid/microwave pre-treatment to the municipal wastewater sludge increased the lipid yield by 91.6% and the biodiesel yield by 160%. On the other hand, for petrochemical industry WWTP sludge, the combined acid/microwave pre-treatment increased the lipid and biodiesel yields by about 63%. The highest lipid yield was achieved by the application of combined acid/microwave pre-treatment to the petrochemical industry WWTP sludge samples.

References

Industrial and Agricultural Wastes as a Potential Biofilter Media for Groundwater Nitrate Remediation

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Keywords: Industrial and agricultural waste, groundwater nitrate, remediation, heterotrophic denitrification

Abstract

Legislative instruments enforce the EU members and candidates to take appropriate measures on integrated waste management and integrated protection and management of water resources. Relevant authorities are trying to increase the re-use of waste and/or the extraction of secondary raw materials and decrease groundwater nitrate concentrations. In this study, two agricultural substances, hazelnut husk and tea factory waste, have been investigated as potential carbon sources to stimulate nitrate removal in low cost permeable reactive barrier (PRB) systems. Leaching and batch experiments were carried out to determine the dissolution level and the degree of heterotrophic denitrification process. Results showed that both wastes support denitrifying populations and if used would result in a reduction in landfilled biodegradable wastes. The percentage of organic substrate played an important role in the removal of nitrogenous compounds. The highest nitrate removal efficiencies were observed in flasks with 40% tea factory waste and 100% hazelnut husk, which were 64 and 97%, respectively. The corresponding zero-order reaction rates were 3.03 mg N L⁻¹ d⁻¹ for tea factory waste and 5.17 mg N L⁻¹ d⁻¹ for hazelnut husk.

1. Introduction

Solid waste volumes continue to increase due to intensive agricultural activities and industrial production. The amount of waste generated in the EU-27 in 2006 is about about 3 billion tonne (EUROSTAT, 2010). Besides prevention and reduction of wastes, the Waste Framework Directive (WFD) (Directive 2008/98/EC) also requires the member states to take appropriate measures for recycling, reuse or reclamation of wastes with a view to extracting secondary raw materials (Pawelczyk, 2005). The EU Landfill Directive, on the other hand, is setting targets for the reduction of biodegradable wastes (bio-wastes) going to the landfill (Council Directive 99/31/EC). Activities have also increased the nitrate concentration in both ground and surface water resources. Health concerns of high contaminant levels in drinking water (e.g. higher risks of methaemoglobinaemia in infants and cancer due to elevated nitrate concentrations (WHO, 1999)) have resulted in the development of legislative instruments for an integrated protection and management of water resources (e.g. Water Framework Directive (Directive 2000/60/EC)). The Nitrate Directive (Directive 91/676/EEC), which is also implemented in Turkey, requires measures for the reduction of nitrate in groundwater. New microbial denitrification strategies have emerged for nitrate removal as more economical, practical and permanent solutions (Schipper et al., 2010b). The aim of this study was to decrease the nitrate concentration in groundwater by simply using the denitrification process. This heterotrophic process requires the presence of an organic source which is necessary for the reduction of NO₃ to N₂. Two
dominant organic wastes in Turkey, tea factory waste and hazelnut husk, were used as potential carbon sources to stimulate nitrate removal in low cost permeable reactive barrier (PRB) systems.

2. Materials and Methods

The aqueous solutions were sampled for NO$_3^-$, NO$_2^-$, NH$_4^+$ and TOC analyses. pH, ORP and DO were determined using Mettler Toledo Seven Multi multi-meter. DO was measured using a portable DO meter equipped with a Hanna HI 9145 electrode. Total organic carbon of each sample was measured in triplicate with a high temperature aqueous TOC analyser (Tekman Dohrmann Apollo 9000). Thermo Scientific Helios Zeta UV/VIS spectrophotometer analysed nitrate, nitrite and ammonium concentration in accordance with methods # 8171, 8153 and 8038 of the HACH water analyses handbook, respectively. Elementar vario MACRO cube CHNS Elemental Analyser was used for the elemental analyses of organic substances. Microorganisms were harvested and genes representing denitrifying organisms (nirS and nirK) and total bacteria (16S rRNA) were quantified by qPCR (Bio-Rad Cycler, Hemel Hempstead, UK) using ssoFastEvaGreen PCR reagents (Bio-Rad; 10 µL reactions) and previously designed primers [nirS: (Kandeler et al., 2006) and nirK: (Henry et al., 2004)].

3. Results

As can be seen from Figure 1, the increased percentages of tea residue resulted in higher nitrate concentrations in solution, whereas for studies using nut husk lower nitrate concentrations were obtained. Thus, the highest nitrate removal efficiencies were observed in flasks with 40% tea factory waste and 100% hazelnut husk, which were 64 and 97%.

![Figure 1. Nitrogen species in the solutes of batch experiments.](image-url)

References


Hexavalent Chromium Removal Using Ion Exchange (IX) Enhanced Capacitive DeIonisation (IX CDI)

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Keywords: electrosorption; Hexavalent Chromium removal; Ion Exchange Enhanced Capacitive Delonization; Wastewater treatment; Activated carbon electrode.

Abstract

The aim of this study was to investigate an ion exchange enhanced CDI (IX CDI). Where, the CDI cell central space, between the activated carbon electrodes, was filled with an IX resin mixed bed; this aimed to drastically reduce the electric resistance of the cell flowing space, as with electrodeionisation (EDI). This IX CDI cell was applied to remove and recover hexavalent chromium (Cr VI) from industrial wastewaters. The IX CDI showed 50 % higher efficiency than conventional CDI. This was the main research finding.

The hexavalent chromium removal by CDI is not a novel finding but its cyclic desorption by current reversal, remained a serious CDI issue; this was successfully solved here, by a chemical regeneration method. The effects of main CDI parameters (pH, voltage, flow rate and concentration) and their optimization were systematically investigated in a batch mode process. The Cr VI removal efficiency was 98 % (from 63 to 1 mg/l) in acidic medium, allowing water recycling;

1. Introduction

CDI is becoming an established, promising and competitive desalination process. The ionic solutes removal is based on an electrosorption effect; under an applied voltage the ions migrate towards the CDI cell electrodes where they accumulate without reacting thanks to a non-faradic or capacitative effect and form an interfacial electric double layer (EDL). The ions removal efficiency is then strongly related to the electrodes properties such as a high specific area and a large electrochemical window. The cyclic current reversal evacuates the electrosorbed ions in a separate concentrated circuit and regenerates the electrodes.

Industrial pollution prevention is another interesting CDI application with versatile and unlimited possibilities. The treated water may be recycled and the pollutant removed, concentrated and recovered in a cleanly process. recently, pollutants removal by CDI is widely studied to remove inorganic compounds and also various organic pollutants.

Various efficiency enhancing methods (CDI with ion exchange membranes MCDI, modified and sophisticated electrodes materials, flow regimes, etc) were largely investigated with sensitive efficiency improvements but with higher costs, sophisticated materials and complicated designs.

This research work proposes an alternative treatment for Cr VI wastewaters; a novel configuration of the capacitive deionization (CDI) process, the ion exchange enhanced CDI (IX CDI) is presented here. Thanks to the activated carbon electrodes inertness towards Cr
VI and the extreme valence of hexavalent chromium, CDI could constitute a robust removal process.

2. Materials and Methods

The Cr (VI) removal by CDI was performed by applying a direct voltage between the GAC electrodes using a single output adjustable DC power supply. This voltage, noted V, measured the total voltage drop, including cell resistances, between the two electrodes; it is not an electrochemical potential as conventionally measured against a reference electrode.

3. Results

Figure 1 shows the C – t curves and removal capacities for AC adsorption, ordinary CDI and IX CDI configurations. The IX introduction has seriously improved the BMCDI efficiency which increased from 5.0 mg/g for adsorption, to 10.95 mg/g for BM-CDI and finally reached 16.3 mg/g for the IX BMCDI. The IX mixed bed, with an ordered configuration, has drastically decreased the electrical resistance of the CDI cell, specifically the central flowing compartment, and increased the ionic mobility in the IX “sandwiched” medium.

![Figure 1: Comparison the concentration – time curves and during the adsorption, BM-CDI, and IX-CDI runs of Cr(VI)]](image-url)

References

Abstract

This research is a preliminary assessment to utilize the liquid smoke resulted from durian peel pyrolysis to preserve fish. This preservation process was conducted by soaking the mackerel sample in 0.5, 1, 2, and 3% liquid smoke concentration levels to be observed every 6 hours. Testing on antibacterial property showed that the liquid smoke can inhibit the growth of Salmonella contained in fish even at a low concentration level. The organoleptic testing showed that the concentration influenced the mackerel sample’s preservation. At 2-3% concentration, the fish sample still possessed acceptable flavor, taste, color and texture up to 48 hours of soaking. However, the best condition was obtained at 3% concentration (of liquid smoke produced at 340°C pyrolysis), in which the fish was still acceptable up to 42 hours. The Total Volatile Base (TVB) testing showed that at 54 hours, the TVB value remained below 30 mgN/g, meaning it was still safe for consumption.

1. Introduction

Indonesia is located at the equator and is rich with abundant plantation produce as well as other natural resources, such as durian. Although seasonal, durian production in Indonesia continues throughout the year. High consumption of durian led to a few environmental issues since there is no proper management of durian peel waste. In general, durian peel contains a high level of cellulose (50-60%), starch (20%) and lignin (Faisal et al., 2018a), making it potential as liquid smoke raw material. The liquid smoke contains phenol, carbonyl and other acid. These compounds have antimicrobial properties that can preserve food; they inhibit damaging and decomposing microbes in food and therefore lengthening the storage duration of food products. In addition, liquid smoke can add to taste, color and unique flavor. Several researchers studied the use of liquid smoke produced from wood biomass to preserve fish, meatball and tofu (Faisal et al., 2018b). Nonetheless, to our knowledge, none of the researches utilized durian peel biomass for preservatives despite the available amount and potential of durian peel waste. This research is aimed at studying the potential of liquid smoke resulting from durian peel pyrolysis as a natural mackerel preservative.

2. Materials and Methods

Liquid smoke was produced in a pyrolysis reactor as explained in previous research (Faisal et al., 2018b). As much as 3 kg of dried durian peel was put into the reactor set at 340°C and 380°C. The resulting smoke was condensed to produce tar, charcoal and liquid smoke Grade 3. The next step was distillation at 190°C to separate liquid smoke from tar, resulting
in liquid smoke Grade 1. This was then used as preservative by soaking fish in different concentrations: 0.5%, 1%, 2%, and 3%. The analysis tests used were TVB and organoleptic.

3. Results
The TVB test results in fish after being soaked in liquid smoke can be seen in Figure 1.

![Correlation between soaking time, liquid smoke concentration and TVB value in fish (liquid smoke was produced at 340°C)](image)

Figure 1. Correlation between soaking time, liquid smoke concentration and TVB value in fish (liquid smoke was produced at 340°C)

Figure 1 show that the higher the liquid smoke concentration, the lower the resulting TVB value is and the more inhibition is produced against bacteria. A 3% liquid smoke has the lowest TVB value. TVB values increase due to an enzyme produced by bacteria to degrade protein into amino acid, and short peptide bond which results in a number of bases such as amine, ammonia, and trimethylamine that cause foul smell. The hedonic test results for flavor and aroma are shown on table 1.

Table 1. The hedonic test results for flavor and aroma

<table>
<thead>
<tr>
<th>Pyrolysis temperature (°C)</th>
<th>Liquid smoke concentration (%)</th>
<th>6</th>
<th>12</th>
<th>18</th>
<th>24</th>
<th>30</th>
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</table>

The liquid smoke can slow down the occurrence of foul smell and bad flavor in mackerel for up to 30 hours. With regards to aroma, the use of 2-3% concentration of liquid smoke produced at 380°C could maintain desirable aroma up to 48 hours of soaking, although it grew thick (similar to the smell of liquid smoke).

References
Ammonia Recovery From Chicken Manure Digestate via Gas Diffusion Tubular Polypropylene Membrane

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Abstract

Biogas production industry has been increasing for the last decade in Turkey. With the anaerobic digestion of high organic matter containing especially agricultural waste and animal waste, stabilization of these wastes can be achieved along with biogas thus energy production. During anaerobic digestion a secondary waste which is called as digestate is generated. Digestate can contain high amount of nutrients such as nitrogen and phosphorus depending on the type of the waste to be digested. The discharge of digestate may cause serious environmental problems especially in case of high ammonia. Hence, ammonia has to removed before discharge.

Some phsico-chemical methods such as ammonia stripping, zeolite adsorption, struvite precipitation, has been abundantly studied in literature. Particularly, there are plenty of ammonia stripping studies. However, given that it contains high concentration of dissolved and suspended solids, ammonia stripping is not applicable, especially in real-scale stripping towers.
Sepiolite Supported Co-Ce-B Catalyst for Hydrogen Generation from NaBH₄

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Keywords: Ce-Co-B catalyst, sepiolite, sodium borohydride, hydrogen

Abstract

In this work, cobalt-cerium-boron/Sepiolite (Co-Ce-B/Sepiolite) catalyst was prepared by impregnation and chemical reduction method. The supported Co-Ce-B catalyst was tested in the hydrolysis of NaBH₄ in alkaline solution. The effects of catalyst amount, NaBH₄ concentration, NaOH concentration and reaction temperature on the hydrogen generation rate were investigated. The cycle test of catalyst was investigated to determine the durability of catalyst. The optimal experimental conditions were determined for hydrogen production. The hydrolysis kinetics of NaBH₄ was also investigated.

1. Introduction

Nowadays, the depletion of fossil fuels and increasing of greenhouse gas emissions and energy demand have attracted increasing attention of sustainable energy. Hydrogen appeared to be a clean energy to replace the fossil fuels [Chang et al., 2014]. At present, hydrogen storage was a critical method to the convenient utilization of hydrogen. Chemical borohydrides are currently attractive as a storage option due to their high gravimetric hydrogen capacities. Among the chemical borohydrides, sodium borohydride (NaBH₄) has a gravimetric hydrogen density of around 10.8 % and has been studied as a promising hydrogen storage alternative. Also, the by-product NaBO₂ of NaBH₄ hydrolysis is environmentally clean and can be recycled for synthesizing NaBH₄ [Wu et al., 2011].

Catalytic strategy is one of the crucial issue for sustainable hydrogen supply from NaBH₄ hydrolysis. Metal borides were studied generally as high efficient catalysts for NaBH₄ hydrolysis and among them cobalt boride based catalysts are more attractive ones owing to its excellent catalytic properties and easy preparation. But Co-B can agglomerate easily in an aqueous solution because of high surface energy and exothermic process of synthesis. The transition or rare earth metals and inert supports materials can be increase the nanoparticle dispersion. In particular, rare earth metals not only enhance the catalytic activity but also increase the resistance of the catalyst [Zou et al., 2018]. In this study, Co-Ce–B catalyst was synthesized using sepiolite as a support material by impregnation-reduction method. The effects of reaction parameters on the hydrogen generation were investigated in detail.

2. Materials and Methods

All chemicals were analytical grade. The sepiolite sample was obtained from Eskisehir and was used as a catalyst support. It was crushed, ground and sieved through a 200 mesh sieve. Sepiolite supported Co-Ce-B catalyst was prepared by impregnation and reduction method, where Co and Ce with the ratio of 1:1 and total metal content 15wt % (Co-Ce / Sepiolite
with total metal) was selected. The mole ratio of NaBH₄ and the total metal atoms was set 3:1 to ensure complete a reduction reaction.

Catalyst testing with sodium borohydride hydrolysis reaction was carried out jacketed-heated in batch reactor. The volume of hydrogen released during the experiment was measured by a water displacement method.

3. Results

The effect of the catalyst amount on the hydrogen generation rate was studied using three different catalyst amounts (30, 40 and 50 mg) at NaBH₄ concentration of 0.7 M and a reaction temperature of 50 °C. As the amount of the catalyst increased, the volume of the generated hydrogen not changed, and the reaction time was decreased from 32 minute to 17 minute (Figure 1a). The effect of the NaBH₄ concentration on the hydrogen generation rate was examined using three different NaBH₄ concentrations (0.41 M, 0.55 M and 0.70 M) at a catalyst amount of 50 mg and a reaction temperature of 50 °C. When the NaBH₄ concentration was increased from 0.41 M to 0.70 M, the generated hydrogen volume was increased from 800 mL to 1350 mL, and also the reaction time was increased from 12 minute to 17 minute (Figure 1b). The effect of reaction temperature was investigated at 30, 40 and 50 °C (Figure 1c). When the reaction temperature increased from 30 °C to 50 °C, the hydrogen generation rate increased from 1999 mL/min.gCe-Co to 10588 mL/min.gCe-Co. The hydrolysis reaction kinetics conformed to the zeroth-order. The activation energy of hydrolysis reaction was found to be 66.76 kJ/mol.

![Figure 1. Effect of a) catalyst amount b) NaBH₄ concentration c) reaction temperature on hydrogen generation rate of NaBH₄.](image)

References


State-of-the-art Technology for the Stabilization of Pb in the Incineration Fly Ash Using Waste Fishbone Hydroxyapatite

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Keywords: MSWI fly ash, Natural fishbone, Apatite II™, Pb stabilization, Hydroxyapatite (HAP)

Abstract

The feasibility of using natural fishbone hydroxyapatite (HAP) and a commercial apatite (Apatite II™) on Pb stabilization in MSWI fly was investigated. Their effects were studied under different L/S ratios and settling periods. The highest Pb removal efficiency reached almost 78% after a 6 h batch process when fishbone dosage was only 10% with L/S 1.5. Apatite II™ was also effective; however, natural fishbone was noticeably more effective.

1. Introduction

Municipal solid waste incineration (MSWI) is vastly used in Japan and many other countries across the world. Fly ash is one of the major products of the incineration process. A noticeable amount of heavy metals (Pb, Zn, Cu, Cd, Cr, Sb etc.) in fly ash leads to its classification as a hazardous waste. Currently, a number of techniques are applied in the world for heavy metal stabilization in fly ash including phosphation, vitrification, solidification by cement, chemical treatment and others.

The present research has been designed to elucidate the role of natural phosphate from biogenic source (fishbone) on Pb stabilization in fly ash. Through phosphation, trace divalent metal ions are immobilized in the matrix of highly stable phosphate minerals that belong to the apatite group with the general formula of Ca₅(PO₄)₃(OH, F, Cl). Exploring the effect of fishbone hydroxyapatite on heavy metals entrapment in fly ash was the main target. The early investigations (Mu et al. 2018a and 2018b) and the present research suggested that fishbone waste might have the potential to be converted to an effective metal stabilizer in fly ash.

2. Materials and Methods

MSWI fly ash was obtained from an anonymous incineration plant and mixed fishbone wastes were collected from the Fukuoka City in Japan. The collected fishbone was ground to the powder state after removing the soft tissues through stepwise washing. The elemental compositions of fly ash and fishbone were measured using X-ray fluorescence technique. The concentrations of elements/ions in the leachate of fly ash from the batch leaching tests under various scenarios were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES). Powder X-ray diffraction (XRD) technique was used to identify the crystalline phases in both fly ash and fishbones. Batch tests were conducted under fishbone/fly ash ratios of 0 and 1:10 by weight and various contact times of 6, 12, and 24 h with two different L/S ratios of 1.0 and 1.5. Similar experiments were conducted for both natural fishbone and Apatite II™.
3. Results and Discussion

The effect of both mix natural fishbone meal and Apatite II™ on the stabilization of Pb in fly ash was explored under different L/S ratios and settling periods as contact time. Batch tests were conducted under fishbone/fly ash ratios of 0 (control group) and 1:10 (test groups) by weight and various contact times of 6, 12, and 24 h with two different L/S ratios as 1.0 and 1.5. The effect of fishbone on Pb stabilization was represented by Pb removal efficiency in the leachate after conducting the leaching test JLT-46. The results of Pb concentration and its removal efficiency in the leachates in the absence/presence of fishbone are shown in Figure 1.

It has been observed that natural fishbone with higher L/S was more efficient than lower L/S (Figure 1). The highest Pb removal efficiency reached almost 78% after a 6 h batch process when fishbone dosage was only 10% with L/S 1.5. However, Pb removal efficiency has reached almost 69 and 74% at 6 and 12 h, respectively, with L/S 1.0. In both L/S ratios, the Pb removal efficiency slightly dropped after 24 h settling period.

Apatite II™ was also effective for Pb stabilization in fly ash. In both L/S ratios, the Pb removal trends were very similar with contact times. However, natural fishbone was more effective (about 1.5 to 2 times) than Apatite II™ as shown in Figure 1. While both L/S and contact time did not show any significant difference that ranged between 68-73% (except L/S 1.5 after 12 h leaching process), in case of Apatite II™, it was evident that in both L/S ratios, contact time was a vital factor for Pb removal, as the 12 h scheme showed about 1.5 times higher than 6 h. Therefore, effective contact time and L/S were important factors for higher Pb removal efficiency.

References

Classification and Determination of Drinkability of Thermal Waters in Erciş and Çaldıran (Van, Turkey)

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Keywords: Drinkability, thermal waters, therapeutic properties, Van, Turkey.

Abstract

The therapeutic properties associated with thermal waters encourage people at spas to drink the thermal spa water. Therefore, this study was carried out purpose of determination of drinkability of thermal waters in Erciş and Çaldıran in Van, Turkey. In this study, the physicochemical parameters (Electrical conductivity, pH, Cl\(^{-}\), HCO\(_3\)\(^{-}\), PO\(_4^{3-}\), SO\(_4^{2-}\), NO\(_3^{-}\), NO\(_2^{-}\), F\(^{-}\), Ca\(^{2+}\), K\(^{+}\), Mg\(^{2+}\), Na\(^{+}\), total hardness and dissolved solids) were determined for 5 thermal spring samples collected from Erciş and Çaldıran in Van, Turkey. The surface temperatures of the thermal water samples varied from 25.8°C to 53.3°C with in-situ measurements. pH values varied from 7.2 to 8.5 (alkaline) and all samples exhibited relatively high salinity brackish waters (DS=1217–3198 mg/L). Total hardness measurements indicated that waters are very hard. In Erciş, Hasanabdal and Taşkapı thermal springs have Na–Cl and Na-Cl-SO\(_4\) characters, respectively. In Çaldıran, Ayrancılar thermal spring has Na - HCO\(_3\) - Cl character and other two thermal springs (Koçovası and Buğulukaynak) have same characters with Mg - Ca –Na -HCO\(_3\). The ratios Na\(^{+}\)/Ca\(^{2+}\), Na\(^{+}\)/Mg\(^{2+}\), and (Na\(^{+}\) + K\(^{+}\))/(Ca\(^{2+}\) + Mg\(^{2+}\)) were high in 80 % of the samples. This indicates the ion exchange process is important, which indicates that most of the thermal waters in the study area had developed over a long period at a depth sufficient to react with the rock. The statistical analysis of the physicochemical data for many samples revealed positive correlation values and positive correlation values enable to good interpretation of the results and reveals the composition of ions in thermal waters. Also, drinkability of thermal waters were examined by using WHO (2011) drinking water standards and various criteria (i.e. DS, TH, genesis etc.) and other standards determined by some researchers. The results show that none of the thermal water samples are not suitable for drinking. Thermal waters shouldn’t be consume for public health.

Table 1. Chemical analyses of waters from Erciş and Çaldıran (Van, Turkey).

<table>
<thead>
<tr>
<th>Location</th>
<th>Sample Number</th>
<th>Herceş-Hasanabdal Village</th>
<th>Erciş-Taşkapı Village</th>
<th>Çaldıran-Ayrancılar Village</th>
<th>Çaldıran – Koçovası Village</th>
<th>Çaldıran–Buğulukaynak Village</th>
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<td>7,53</td>
<td>7,74</td>
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<td>Conductivity (μs/cm)</td>
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<td>4620</td>
<td>3800</td>
<td>3420</td>
<td>1696</td>
<td>1155</td>
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<td>Temperature (°C)</td>
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<td>Mg-Ca-Na- HCO\textsubscript{3}</td>
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Figure 1. Location of the thermal waters in the study area.
Recycling of gallium from gallium nitride waste of LED industry by hydrometallurgical method

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Keywords: Gallium, Gallium Nitride, LED Industry Waste, Recycling, Leaching, Ion Exchange,

Abstract

In recent years, with the rapid development of LED and semiconductor industry, it is a major issue to deal with a large number of the related waste containing GaN. Especially the gallium has extremely high economic value, it is necessary to establish the recycling system of the GaN waste. Therefore, a recovery process of gallium has been studied. The process was arranged to leach the valuable metals from the GaN waste and adsorb the gallium from aluminum by ion exchange resin. In the leaching step, different parameters influencing the leaching efficiency of the gallium were investigated, such as various leaching methods, different acid agents of concentration, liquid-solid ratio, reaction temperature and reaction time. In the ion exchange process, in order to optimized the separation of gallium and aluminum, different type of ion exchange resin, the pH value, solid-liquid ratio, reaction temperature, reaction time and the different desorbent which affect the adsorption of gallium were discussed. In the leaching step, the GaN waste was dissolved in hydrochloric acid by pressure leaching in an effective way to the leaching efficiency of gallium. In the ion exchange process, the gallium and aluminum were separated by AMBERLITE IRC748 resin, and used AMBERLITE 200C Na resin to extract and adsorb the gallium. With the optimal conditions, the recovery of gallium could be up to 99.9% after desorbing by acid. After separation, the gallium was purified by precipitation and calcination as metal oxides with the purity over 99% and could be recycled to the industrial for raw material effectively.

1. Introduction

Gallium is essential ingredients for semiconductors and LED chips, cell phones, photovoltaic generation panels, optical communication devices and computers. Gallium is vital for the electronics industry because of its unique physical and chemical properties, are classified as significant from industrial application and critical from supply chain scarcity prospective. According to a recent report published by the united nations environment programme (UNEP), less than 1% of EOL gallium bearing materials being recycled.

The GaN is a crystal of high bond energy that is equal to 7.72 eV/molecule, which results in higher melting temperature and good thermal stability. GaN is employed principally in the manufacture of LEDs and laser diodes, power electronics, and radio-frequency (RF) electronics. Because GaN power transistors operate at higher voltages and with a higher power density than GaAs devices, the applications for advanced GaN-based products are expected to increase in the future. High refractive index, mechanical stability, high heat capacity, and thermal conductivity make the GaN, a material of interest as
semiconductor material, which make GaN, either from the LED industry waste or from EOL GaN-bearing devices, difficult to treat and recycle. Recovery of gallium from the gallium rich LED waste reported in literature are vary scarce, so it is important to develop and establish the recycling system from GaN waste and the hydrometallurgy process can be a solution to the issue.

2. Materials and Methods

2.1. Materials

The sample of GaN waste from LED industry was used for the experiments.

2.2. Acid leaching

The GaN waste was leaching by HNO\textsubscript{3}, H\textsubscript{2}SO\textsubscript{4}, HCl and HF for the best acids selection.

2.3. Analytical procedures

X-ray fluorescence analyzer (XRF, Spectro XEPOS) for semi-quantitation analysis. The scanning electron microscope (SEM, Hitachi, S-3000N) and energy dispersive X-ray spectrometry (EDS) analyze the composition. The concentration was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Varian, Vista-MPX).

2.4. Ion exchange resin

Amberlite® XAD®-2, Amberlite IRA200C(Na), AMBERLITE IRC748 were used for ion exchanger.

3. Results

<table>
<thead>
<tr>
<th>Acid agent</th>
<th>H\textsubscript{2}SO\textsubscript{4}</th>
<th>HCl</th>
<th>HF</th>
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<td>Leaching efficiency of Ga(%)</td>
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<td>3.16</td>
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<table>
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<th>Acid agent</th>
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<th>HCl</th>
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<tr>
<td>Leaching efficiency of Ga(%)</td>
<td>1.36</td>
<td>3.28</td>
<td>8.9</td>
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</table>

Table 1. The leaching efficiency of gallium from different acids at 25°C

Table 2. The leaching efficiency of gallium from different acids at 100°C

References


The Effect of ZrMOF Types on Gas Permeability Properties of PEBA Mixed Matrix Membranes

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Keywords: Gas permeability, mixed matrix membrane, ZrMOFs, PEBA, Polymer nanocomposite

Abstract

There is an increasing interest in the use of membrane gas separation technologies for the separation of H₂ and CO₂ from gas mixtures for various applications such as increasing the quality of natural gas, recycling of waste gas, H₂ production, improved oil production and prevention of global warming. Most of the research is directed towards the development of new membrane materials and structures that exhibit high selectivity and permeability. Mixed matrix membranes (MMM) containing metal-organic frameworks (MOFs) have attracted large attention owing to the combined advantages of high separation performance and easy processability. Polyether block amide was used in this study. By using this matrix, different polymer/MOF nanocomposite membranes were prepared using zirconium based MOFs which will be synthesized with different organic ligands. In this study, the permeability of nanocomposite membranes were examined for pure H₂, CO₂ and CH₄ gases and their ability to separate binary gas mixtures were studied. The effects of MOF structures on gas separation properties and morphology of nanocomposite membranes was investigated. MOF species morphology of the synthesized membranes was examined by the scanning electron microscope (SEM). TGA and differential scanning calorimeter (DSC) analysis were took place for the polymeric membranes. The characterization of synthesized MOFs was analyzed by XRD and BET which is used for surface characterization.

1. Introduction

The gas separation principles for the nonporous polymeric membranes were used rather than the other membrane separation methods. Materials research on gas separation membranes has made considerable progress due to widespread research efforts within industry. One of the most important issues facing the chemical industry is how to separate mixed gases into its components purely. This issue can be solved with the help of membrane technology. Membranes are defined as semipermeable equipment that can permit the passage of one component of a mixture of gases when preventing another component under a certain driving force. The most common practiced separations are production of nitrogen and oxygen enrichment from air, separation in the petrochemical industry and removal of carbon dioxide from natural gas. In addition to the good separation performance, polymeric membranes perform thermal and chemical stability. The gas separation membranes mechanism consists of 3 stages for gas transport through the polymers. The first stage is adsorption of gas molecule on the high pressure side, the seconds stage is diffusion across the membrane, the last stage is desorption on the low pressure side of membrane which is downstream[1,2]. Mixed matrix membrane (MMM) application of gas separation has been considered most of the industry. These membranes are heterogeneous membranes which consist of polymer matrix and inorganic fillers. Organic ligands with a wide range of functionalities are able to make metal organic frameworks (MOFs) to interact very strongly with polymer chains. The first MOF based MMMs was synthesized in order to optimize CH₄ selectivity. Zeolitic imidazolate frameworks are subset of MOFs that consist of transition metal linked to imidazole ligand [3,4].
2. Materials and Methods

In this study, poly(ether-b-amide) (PEBAX®1657, Archena) was chosen as matrix materials of the membrane (Fig.1). PEBA resin; a thermoplastic elastomer made of rigid polyamide segments and flexible polyether segments, is best known under the trademark PEBAX. PEBAX block copolymers, have been investigated for gas separation properties and have shown a nice potential for CO\textsubscript{2} separation. Gas pass through the soft amorphous polyether block and the mechanical stability of the membrane material is provided by the hard polyamide phase.

Figure 1. Chemical structure of PEBA.

To fabricate the mixed matrix membranes, ZrMOF, ZrFUM and ZrMim nanocrystals were synthesized by the solvothermal method. The structures of the Zr-based MOF nanocrystals are presented in Fig.2.

Figure 2. SEM images of ZrMOF nanocrystals.

For PEBA/ZrMOF, PEBA/ZrFUM and PEBA/ZrMim membranes, a certain amount of Zr-based MOF nanocrystals were ground and dispersed in ethanol and water mixed solvent followed by sonication. Then, PEBA were added into the dispersion containing Zr-based MOF nanocrystals. The mass ratios of PEBA to solvent is 5:95 while the contents of Zr-based MOF nanocrystals in polymer matrix were varied from 10 to 30 wt. %.

3. Results

The effects of ZrMOF, ZrFUM and ZrMim loading on gas permeabilities of MMMs were investigated. The morphologies of the membranes were determined with SEM images. Gas permeability of PEBA based MMMs for H\textsubscript{2}, CH\textsubscript{4} and CO\textsubscript{2} pure gases were measured at 3 bar feed pressure and 35°C. For all membranes, the CO\textsubscript{2} permeability was measured more higher than H\textsubscript{2} and CH\textsubscript{4}. The selectivity of CO\textsubscript{2}/CH\textsubscript{4} for PEBA/ZrMim membrane is quite good compared to the other membranes. As the permeabilities of PEBA/ZrMim membranes were compared with other membranes, it was observed that the CO\textsubscript{2} permeability increased in the PEBA/ZrMim membranes according to PEBA/ZrMOF and PEBA/ZrFUM membranes for all Zr-based MOF contents. CO\textsubscript{2}/CH\textsubscript{4} gas permeation tests revealed that the separation properties of mixed-matrix membranes prepared with three different type of Zr-based MOFs, especially selectivities, were improved compared to those of pure polymeric membrane owing to the selective CO\textsubscript{2} uptake and transport in three types of Zr-based MOF nanocrystals.

References


ZrO$_2$ supported on Bamboo Leaves Ash as Heterogeneous Catalyst in Microwave-Assisted Biodiesel Conversion

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$^c$ Chemistry Department, Universiti Tunku Abdul Rahman, Perak, Malaysia

Keywords: Bamboo Leaves, Biodiesel, Zirconia, Heterogeneous Catalysts

Abstract

In this research, Bamboo leaves ash was utilized as ZrO$_2$ support for heterogeneous catalyst application. The preparation of ZrO$_2$ supported Bamboo leaves ash (ZrO$_2$/BLA) was conducted by impregnation method, with the metal content of 10%wt. The physicochemical characterization towards prepared material was studied by XRD, gas sorption analyzer, FTIR and SEM-EDX. The material was tested in biodiesel conversion of soybean oil under microwave-assisted conversion. The results show that physicochemical character of ZrO$_2$/BLA facilitated the catalytic activity in biodiesel conversion. Study on the effects of reaction method, methanol to oil molar ratio, and catalyst weight were investigated. The microwave-assisted method gives comparable yield with reflux method at shorter time. The optimize condition of fatty acid methyl ester (FAME) production is using microwave-assisted reaction, 15:1 methanol to oil molar ratio, 30 minutes of reaction time and 12%wt. catalyst weight. The catalyst shows reusability properties as indicated by the relative similar yield, initial rate and turnover frequency of the process utilizing fresh and reused catalyst.

1. Introduction

Bamboo is considered as one of the fast growing and high in variety plant in Indonesia. Until now, Bamboo plant is natural resource which is mainly utilized for construction, household appliances and also handicrafts purposes particularly from its stem and fiber. From the processes, Bamboo leaves is a waste, meanwhile, chemically, Bamboo leave is rich in silica and other minerals usefull for some applications either in construction or environmental applications. Similar to rice husk ash (RHA) that is widely studied as silica source, BLA has 30-50% of SiO$_2$ in mature leaves. In this research, Bamboo leaves ash was utilized as ZrO$_2$ support for heterogeneous catalyst application. Refer to some researches concerning with the utilization of waste materials, this work reported novel material based on waste from plant(Singh and Sharma, 2017). the purpose of the present research was to develop a low cost and stable heterogeneous catalyst using ZrO$_2$ and BLA for an effective catalytic process of biodiesel production. Preparation, characterization and catalytic activity of ZrO$_2$ supported on BLA composite material (termed ZrO$_2$/BLA) in the MW-assisted process were studied(Guo and Fang, 2011).

2. Materials and Methods

Materials: Bamboo leaves were obtained from Apus Bamboo plant cultivated in Klaten, Central of Java, Indonesia. Bamboo leaves ash (BLA) was prepared by calcining Bamboo
leaves at 400°C for 2 h. Soybean oil was purchased from PT. Indofood Sukses Makmur, Indonesia.

**Preparation of ZrO\textsubscript{2}/BLA Catalyst**

The precursor solution of ZrO\textsubscript{2} was made by dropping ZrOCl\textsubscript{2} solution into water:isopropanol (1:1) solvent followed by stirring for 2h. ZrO\textsubscript{2}/BLA Composite was prepared by mixing the suspension of BLA and ZrO\textsubscript{2} precursor solution followed the addition of HCl 0.01M and reflux for 4h. Theoretical Zr content was set up at 10% wt. respect to BLA. The mixture was then dried in an oven at 60°C before calcination at 400°C for 4h.

3. Results

![Kinetics of biodiesel conversion](image)

**Figure 1.** Kinetics of biodiesel conversion by (a) MW-assisted method (b) reflux

Kinetics of biodiesel production over ZrO\textsubscript{2}/BLA compared with BLA was studied in varied methods: reflux method and microwave-assisted method. The kinetics curve is depicted in Fig. 1.

Biodiesel obtained from MW-conversion over BLA has higher CN value than 60 while biodiesel produced by other method present CN lower than 60. Further analysis toward GCMS results indicates that the composition of biodiesel obtained by BLA under MW assisted conversion consist of dominantly methyl palmitic and methyl lauric while other biodiesel samples composed by methyl palmitate. The predicted CN values of the obtained biodiesel over ZrO\textsubscript{2}/BLA catalyst have already fulfilled the ASTM standard. According to ASTM D-1298, the predicted cetane number was less than 60.0, indicating that the produced biodiesel was very suitable for engine performance. This cetane number was mainly affected by high composition of methyl oleate (9) and methyl palmitate (C16:0).

References


Enhancing the effectiveness of methylene blue (MB) phodegradation by ion Cu$^{2+}$ doped to magnetic-photocatalyst (Fe$_3$O$_4$/TiO$_2$)

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$^2$ Chemistry Department, Gadjah Mada University, Sleman, Indonesia

Keywords: photodegradation, methylene blue, dyestuff, wastewater, magnetic-photocatalyst

Abstract
Magnetic-photocatalyst preparations doped with transition metal ions have been successfully performed. The aim of this study is to prepare a reusable post-treatment photocatalysts and that have high photocatalytic effectiveness under visible light. The result of characterization with XRD indicates that magnetic material has been formed and that 20 angular shift indicates doping success. The synthesized material is spherical in form as shown by SEM result. The results of the activity test showed the doped magnetic-photocatalyst (Fe$_3$O$_4$/TiO$_2$-Cu) having the highest activity in degrading the blue methylene of 97.03% under visible light radiation and under UV light radiation are 92.64%.

1. Introduction
Synthetic dyestuff have been used widely in various fields both in home industries and national scale industries. Colored wastewaters is a dramatic source of pollution in aquatic life (Houas et al, 2001). This contaminants may exhibit toxic, carcinogenic and such present a serious hazard to humans (Ljubas et al., 2015). To overcome this condition, photodegradation was proposed as an excellent method. TiO$_2$ is a photodegradation agent that is widely used due to its photocatalytic activity. However, the disadvantage of using TiO$_2$ fine powder is that it is easily dissolved during the treatment so it can not be reused. Providing magnetic capability by attaching it to a magnetic materials such as Fe$_3$O$_4$ can make the photocatalyst recovered after treatment (Yang et al., 2009 and Banisharif et al., 2013). Another disadvantage of TiO$_2$ photocatalyst is its weak activity under visible light, while 45% of the rays come to the earth are visible lights. To increase the activity, doping with an economical transition metal ion can be performed (Yang et al., 2015 and Bashiri et al., 2015). This work proves that doping with one of the transition metal ions (Cu$^{2+}$) can improve the effectiveness of methylene blu dyestuff photodegradation under visible light radiation.

2. Materials and Methods
Materials
Iron(III) chloride hexahydrate (FeCl$_3$.6H$_2$O), Iron(II) sulfate heptahydrate (FeSO$_4$.7H$_2$O), ammonia hydroxide 25%, ethanol 98%, sodium citrate, tetraethyl orthosilicate (TEOS), titanium(IV) isopropoxide (TTIP) 97%, Copper(II) nitrate (CuNO$_3$), all reagents are pure grade obtained from Merck.

Methods
This work includes 3 steps, the first is Fe$_3$O$_4$ synteisis with the precursor of Iron(III) chloride hexahydrate and Iron(II) sulfate heptahydrate through co-precipitation process under alkaline condition and under nitrogen flow, the second, coating Fe$_3$O$_4$ with SiO$_2$ synthesized
using Strober method and the third is coating the Fe₃O₄/SiO₂ with TiO₂ which is also at once doping with Cu²⁺ ion through sol gel method.

3. Results
This work was conducted with the primary aim of preparation a reusable post-treatment photocatalysts that have high photocatalytic effectiveness under visible light. The XRD characterization of Fe₃O₄/TiO₂-Cu is shown on Fig.1.

As shown by Fig 1, there are the same characteristic peaks of Fe₃O₄/TiO₂-Cu with the pure TiO₂. Taking the highest intensity peak (2θ), namely 25.38; 38.7; 48.54; 54.06; 55.2 and 62.88, it confirmed that TiO₂ crystal in anatase form has been successfully synthesized. The existence of magnetite (Fe₃O₄) has shown by the respective characteristic peaks (2θ); 30; 35; 57; 62.

As characterized by SEM instrument, the form of synthesized photocatalysts are spherical as shown by Fig 3.
The slow process of magnetite synthesis significantly determines the sphere shape of the photocatalyst. The synthesis process carried out by the sonicator also determines the homogeneous form of the material. As shown by the Fig 2, the average size of Fe₃O₄/TiO₂-Cu are 1 µm. Small size photocatalyst particle can contribute to increased photocatalytic activity due to its large surface area.

![Graph of MB degradation under visible light radiation](image)

![Graph of MB degradation under UV light radiation](image)

Figure 3. Percentage degradation of MB under: a) visible light radiation and b) UV light radiation

The activity test under visible light radiation demonstrates that Fe₃O₄/TiO₂-Cu has higher activity than non-doped photocatalyst. The percentage of degradation MB by Fe₃O₄/TiO₂-Cu under visible light are 97.03% and under UV light radiation are 92.64%. The non-doped photocatalyst used are Fe₃O₄/TiO₂ and TiO₂, the two non-doped photocatalyst show lesser percentage than the doped photocatalyst.

References


Removal of Cu(II) ion from aqueous solution by activated carbons produced from banana fruit bunch (*Musa paradisiaca*)

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Telp: +628112551896

Keywords: Banana fruit bunch, activated carbon, metal ion, NaOH activating agent, Hydrothermal

**Abstract**

Banana fruit bunch is a solid waste collected at open area around the industry. Three types of activated carbons were prepared from banana fruit bunch using different concentrations of NaOH as activating agents and under low hydrothermal carbonization method. Experimental results showed that the maximum surface area was obtained at concentration 20% NaOH of 33.43m²/g. Surface morphology of activated carbon have the network cavities of mesopores structures with unsmooth surface, irregular size pores, and it was covered with the residue of raw material such as carbon and silicon. Surface chemistry of activated carbon showed a highly oxygen-functional group elating with based properties. The absorption of metal ion, Cu (II) was significantly affected by the initial pH of solution, concentration, contact time and mass of adsorbent. Equilibrium adsorption capacity was evaluated using the Langmuir and Freundlich isotherm models. The correlation coefficients (R²) of Langmuir and Freundlich isotherm were obtained 0.9267 and 0.9401, respectively. The result of this observation showed that activated carbon is efficiently used as adsorbent for removal of Cu (II) in aqueous solution.

**Research outline**

Banana is an edible fruit that one of the most popular fruit all over the word. It is considered to have high vitamin and mineral. Banana plant can be separated into trunk, leaves, fruit and empty fruit bunch. Banana fruit bunches do not use for many purposes and are mostly dumped as solid waste at open area. It might cause a real environmental problem such as air pollution by producing unpleasant odor. It is sneccessary to find a technology treatment for protect environmental problem and enhance toward zero pollution.

Activated carbon is defined as a highly porous material with excellent properties such as surface area, pore volume, pore size distribution and chemical surface. These properties become a basic requirement for an adsorbent to enhance the highly adsorptive capacity. The utilization of activated carbon is mainly used for separation and purification process such as removal of organic or inorganic impurities from liquid and gas phase.

Preparation of activated carbon can be considered into 3 parts: selected the raw materials, chemical activation and carbonization process. Raw materials with high carbonaceous compounds are used for activated carbon production. Recently, large of agricultural by-product obtained at open area become a serious waste that can intimidate a damaged environment. Development of agricultural by-product as alternative raw material for activated carbon is important to study. Previous works reported that banana fruit bunch is
good alternative of raw materials and gives a good prospect such as reducing environmental problem, increasing the economic value of waste and low cost raw material. However, the characteristics and applications of the banana fruit bunch as adsorbent are still limited.

In general, preparation of activated carbon used chemical activation as activating agent such as sodium hydroxide. The penetrations of activating agent into the matrix carbon structure of raw material have supported to accelerate the formation pore structure. In general, raw material is carbonized at high temperature ranging from 500 to 1000°C and produced poor surface functional groups. Recently, preparation of activated carbon focused on low temperature carbonization in range of 250 – 400°C. Carbonization using Hydrothermal process is preferred as the gaseous oxidizing is better diffusion, react with carbon to form surface functional group and develop well-pore structure.

The main objective of this research is to evaluate the ability of activated carbons prepared from banana fruit bunch for removal of Cu (II) ion aqueous solution. Characterization of pore structures was analyzed by Gas Sorption Analyzer. Surface Morphology was imaged by Scanning Electron Microscopy-Energ and Dispersive X-Ray (SEM-EDX). Surface functional groups were determined by Fourier Transform Spectroscopy Infrared (FTIR). Amount of Cu (II) ion removal was calculated by the the Asorption Atomic Spectroscopy. The results showed that

Three types of banana fruit bunch activated carbons were well investigated. Experimental data show that activated prepared at 20% NaOH have the highest BET surface area of 33.43m²/g. The presence of hysteresis loop in the nitrogen isotherms curves clearly seen as the heterogeneous mesopores structure. Surface morphology images obviously show the effects of sodium hydroxide by exhibiting the network cavities of mesopores structures with unsmooth surface and irregular size pores. Evaluation of adsorption capacity of activated carbon was carried out for removal of Cu (II) ion in the aqueous solution using the Langmuir and Freundlich isotherms models. Both models indicated the best correlation coefficients (R²) 0.9267 and 0.9401 for Langmuir and Freundlich isotherm, respectively. The result can be resumed that banana fruit bunch activated carbon is efficiently used as adsorbent for removal of metal ions.
Optimization of Dilute Acid Hydrolysis of Kitchen Wastes for Bioethanol Production

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Keywords: Renewable energy, Biomass, Municipal solid waste, Kitchen waste, Acid hydrolysis

Abstract

An increase in energy consumption due to rapid industrialization and exponential growth in the population has caused a decline in fossil fuel reserves. Therefore, there is a great interest in exploring alternative energy sources like biofuels and etc. Biofuels have been produced industrially by fermentation of sugars derived from agricultural residues like a wheat, corn, sugar beets, sugar cane and molasses. But because of economic, moral and environmental issues an efficient substrate must be used for bioethanol production. For this reason, one of the sources that best serve the purposes identified as municipal solid wastes (MSW) like a kitchen wastes (KW). KWs and other organic wastes that are used as an alternative energy source all over the world are used for bioethanol production. Kitchen waste, renewable and low-cost nature resource, isn’t used industrially.

In this study was to examine of the saccharification by the dilute acid hydrolysis of kitchen waste for the production of fermentable sugars. Kitchen wastes were treated with sulfuric acid, (H₂SO₄), for varying periods (0-90 min), with varying acid concentrations (0-5%, w/w) and constant sample concentration (1/10 solid/liquid ratio). Kitchen waste which was solid biomass waste, was treated with steam before and after dilute acid pretreatment, at 121°C increasing residence times (30, 60 and 90 min). The sugar composition of the hydrolyzed kitchen waste which was pretreated with best saccharification method obtained from this study, was analyzed using thin layer chromatography (TLC). The reducing sugars in the hydrolyzate were determined by the DNS method at 575 nm using D-glucose as the standard.

As a result; acid hydrolysis of KWs with H₂SO₄, showed that the amount of soluble sugars obtained could be increased up to the levels of total sugars. Additionaly, we were observed of steam pretreatment which was combination with acid hydrolysis, has positive affect on the formation of soluble sugars.
Environmental Sensitivity of Printed Circuit Board (PCB) Manufacturing to Transportation, Cu Recycling Rate and Energy Source Variations

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Keywords: Printed circuit board; electronics industry; life cycle assessment; Cu recycling; transportation; energy source.

Abstract

Electronics sector is the most rapidly growing sector on a world wide basis. On the other hand, printed circuit boards (PCBs) are indispensable parts of all electrical and electronic devices. In this respect, the production of PCBs that is well known by their negative impacts on environment, requires a special attention. Life cycle assessment (LCA) provides a holistic perspective on impacts by covering all the processes and operations about a product. Therefore incorporating LCA studies to get the whole picture for such products are essential.

This study concentrates on environmental impacts of PCB manufacturing. The objective is to find out the effect of transportation, Cu recycling rate and energy source on various impact categories of global warming potential (GWP), acidification potential (AP), marine aquatic ecotoxicity potential (MAEP), freshwater aquatic ecotoxicity potential (FAEP), ozone layer depletion potential (ODP), terrestriec ecotoxicity potential (TETP), photochemical ozone creation potential (POCP), abiotic depletion fossil (ADP fossil), abiotic depletion elements (ADP elements), eutrophication potential (EP), human toxicity potential (HTP). The transportation of inputs such as fabricated board and chemicals to the factory; together with the waste transportation to end-of-life disposal are considered. Two different Cu recycling rates of 30 \% and 47 \% are evaluated in terms of their effects on impacts. Moreover, usage of renewable energy sources rather than grid electricity is also appraised.

LCA modelling is performed by using Ecoinvent integrated GaBi software, while CML 2001 (Guinée et al. 2001) method is adopted for the calculation of environmental impacts. The results are presented by using a functional unit of 1 m\textsuperscript{2} ready-to-use PCB.

References


Production of Levulinic Acid From Biomass With Using Recyclable Magnetite Solid Acid Catalysts

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Keywords: Levulinic acid, magnetite solid acid catalysts, biomass.

Abstract

Valorization of renewable resources have become popular in many areas due to environmental issues and the rapid depletion of non-renewable resources in the globalizing world. Biomass is the only renewable resource of fixed carbon, which is essential for the production of liquid hydrocarbon fuels and value-added chemicals. Levulinic acid, identified (National Renewable Energy Laboratory, Denver, USA) as one of a number of key sugar-derived platform chemicals, can be used for synthesis of bio-chemicals including succinic acid, resins, polymers, herbicides, pharmaceuticals and flavouring agents, solvents, plasticisers, anti-freeze agents and biofuels/oxygenated fuel additives (Rackemann and Doherty 2011). It could be obtained from maleic anhydride and furfuryl alcohol but the industrial conversion routes are more complex than the acid hydrolysis of biomass and result in the relatively high market price of levulinic acid. In this case, the cellulosic/lignocellulosic biomass have become more preferable as a cheap and abundant raw feedstock material. Magnetite-solid acid catalysts are frequently used in biomass conversion due to the easy separation from solution media and durability on high reaction temperatures. In this study, magnetite halloysite nanotubes (HNTs) and multiwalled-carbon nanotubes (MWCNTs) were used as catalyst support and acidity was provided by sulphonation. Catalytic conversion of LA was carried out by using synthesized catalysts at optimum conditions (200°C for 1 hour) from the hydrolysates of waste biomass materials; corn straw and cotton linter and cellulose as model compound. The quantities of LA were determined by HPLC and the characterization of the catalyst was carried out by physisorption of N2, FTIR, ICP-OES and elemental analysis methods. It was observed that sulphonated magnetite halloysite nanotubes showed higher catalytic activities for dehydration of monosaccharides in corn straw hydrolysate to LA. Magnetite solid acid catalysts made the process environment-friendly and low cost due to the easy separation of catalyst.

References

Shale gas extraction by hydraulic fracturing and flowback treatment technologies from shale gas extraction: A review

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Keywords: Shale gas, hydraulic fracturing, shale gas wastewater, flowback, wastewater treatment

Abstract

Shale gas is a natural gas considered as a new source of energy worldwide and shale gas extraction begins in the 2000s through the use of horizontal drilling and hydraulic fracturing methods leading to a decrease in the price of natural gas and oil globally. Hydraulic fracturing and shale gas production lead to several environmental problems and social concerns including atmospheric pollution, freshwater consumption and water pollution, traffic and noise pollution. Hydraulic fracturing requires large amounts of fresh water, suspended sand called proppants and chemicals. Millions liters of water are needed during the hydraulic fracturing phase of extraction which is a very important topic in water management. This paper reviews the shale gas extraction and production via horizontal drilling and hydraulic fracturing methods, flowback characteristics, reuse and possible treatments of flowback produced from shale gas extraction in order to minimize their environmental risks.
Synthesis of the Iron Nanoparticles by Using Pinus brutia Extract and Hydrogen Gas Production During the Synthesis

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Keywords: accumulator plant, leach solution, hydrogen production, iron nanoparticles, Pinus brutia, sodium borohydride

Abstract

In the present work, both the iron nanoparticles by the chemical reduction method were synthesized and the hydrogen gas was produced during the reaction. In the nanoparticle synthesis method, the leach solution prepared from the branches and leaves of Pinus brutia, iron accumulator plant, was used as an iron source and NaBH₄ was used as the reductant agent. The synthesized iron nanoparticles were characterized by UV-vis spectrophotometer, XRD, SEM, and EDX. The amount of the generated hydrogen gas was measured by the volume of the displaced water. Besides, the effects of temperature, pH, NaBH₄ amount, and PVP amount on the hydrogen gas production were investigated.

1. Introduction

In the literature, different types of metallic nanoparticles have been synthesized by chemical reduction method. In the typical chemical reduction method, metal cations in the synthetic metal salt solutions are reduced by the reductant agents [1]. Differently from the literature, in the present work, a leach solution prepared from the branches and leaves of an accumulator plant is used as the metal cation source in the nanoparticle synthesis. Pinus brutia (Calabrian pine) is known as an iron accumulator plant; so, by using NaBH₄ as the reductant agent and the leach solution containing iron cations prepared from P. brutia, iron nanoparticles could be synthesized in this study. During the synthesis reaction, both of the formation of the nanoparticles and the release of hydrogen gas are take place simultaneously. In the literature, the hydrogen gas production has been carried out by mostly catalytic hydrolysis of various hydrides (KBH₄, LiBH₄, and NaBH₄) in presence of heterogeneous catalyst [2]. But, this production method requires the use of catalysts, whose synthesis methods are difficult and costly. Thus; in this study, it has been firstly focus on evaluating of hydrogen gas released during the synthesis of a nanoparticle and also using a leach solution as metal source in a nanoparticle synthesis.

2. Materials and Methods

Preparation of Leach Solution from Pinus brutia: Pinus brutia (Calabrian pine), known as an accumulator plant, was provided from the vicinity of the chromite (FeCr₂O₄) stratum in Musali district of Mersin province. In order to determine the component accumulated in P. brutia; the leaves and branches, which were purified from impurities and dried, were firstly weighed in certain amounts and then they were burned in porcelain crucibles in a muffle furnace at 550 °C for 10 h. Ash samples were then cooled and weighed. After that, the certain volume of concentrated HNO₃ solution were added to the ash samples and HNO₃ solution was evaporated by using hot-plate until the ash samples dry. The residues were re-dissolved in the certain volume of concentrated HCl and diluted to desired volume by adding distilled water [3]. The contents of the leaching solution were analyzed by ICP-MS. Accordingly, it was observed that the leach solution contained 13.81 mg/L iron (3452.5 mg
Fe/kg plant) whilst the other components were in relatively low concentrations compared to the iron. This suggests that *P. brutia* can accumulate iron element in itself higher than the other components.

**Nanoparticle Synthesis and Hydrogen Gas Production:** In the nanoparticle synthesis; the certain amount of NaBH₄ was added to the as-prepared leach solution (20 mL) into the 100 mL-erlenmeyer flask sealed with stopper and connected with the inverted-placed and water-filled volumetric cylinder. In this system, the iron cations in the leach solution were reduced to iron nanoparticles with BH₄⁻ ions and simultaneously, hydrogen gas was produced during the nanoparticle synthesis reaction. The amount of the generated hydrogen gas was measured by water displacement method [4].

**Nanoparticle Characterization:** The characterizations of the nanoparticles were carried out with UV-vis spectrophotometer, XRD, SEM, and EDX methods.

**3. Results**

The results of the iron nanoparticle synthesis and hydrogen gas production during the nanoparticle synthesis were given below:

- With UV-vis spectrophotometer, the maximum absorption peak for the black colored solution containing iron nanoparticles was obtained at 300 nm of wavelength. The characteristic absorption peak for the synthesized nanoparticles is consistent with the results of the studies on the iron based nanoparticle synthesis in the literature. According to XRD pattern; the synthesized nanoparticles have characteristic peaks belonging to Fe₃O₄ (magnetite), FeOOH (goethite), γ-FeOOH (lepidocrocite), Fe⁰ (zero valent iron) and NaCl phases. SEM images showed that the synthesized particles were in nanoscales and porous structures.

- The effects of temperature (30-65 °C), pH (natural, 3.0-9.0), NaBH₄ amount (0.7-2.5 g), and PVP amount (0.1-2.0 g) on the hydrogen gas production were investigated. The results showed that the volume of hydrogen gas increased with increasing pH, temperature, and NaBH₄ amount; also, it increased with increase in PVP amount up to 1.0 g and thereafter, it relatively decreased by increasing of PVP amount to 2.0 g. Moreover; the separately addition of PVP and NaBH₄ and also the increasing of pH as well as the decreasing of temperature caused the extension of the reaction time. Accordingly; the maximum hydrogen volume of 6000±50 mL was achieved in 80 min in presence of 1.0 g PVP and 2.5 g NaBH₄ at 65 °C and pH of 9.0.

Consequently; by using leach solution, which was prepared from an accumulator plant (a green source), and NaBH₄; it is possible to synthesize iron nanoparticles which can be widely used in many fields such as wastewater treatment, catalyst applications, antibacterial applications, sensor applications, and also simultaneously to produce hydrogen gas, an alternative energy source.

**References**


Effect of Seed Biomass on Wastewater Treatment Performance

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Keywords: activated sludge, filamentous organisms, inoculum, modelling, respirometry

Abstract

Two lab scale sequencing batch reactors (SBRs) initiated with different seed biomass obtained from two different municipal wastewater treatment plants in order to compare the effect of initial seed sludge composition on the treatment performance. The overgrowth of filamentous microorganisms was observed in SBR-1 after 70 days of operation resulted in a sludge volume index (SVI) of 265 mL/g. Whereas the dominance of filamentous microorganisms observed in the raw seed sludge was decreased in SBR-2 (SVI 160 mL/g). The effluent soluble COD in SBR-1 and SBR-2 were 70 and 40 mg/L, respectively.

1. Introduction

The efficiency of an activated sludge process depends on a good solid–liquid separation, which is strongly determined by the activated sludge settling properties. Settling properties depend mainly on the flocs’ structural properties and dominant microbial population. It was reported that during the long term operation of a pilot scale sequencing batch reactor (SBR) different microbial community structures and floc structures can be observed (Govoreanu et al., 2003). Correlation between floc structure and settling properties is highly dependent on the type of microorganisms present in the floc structure and dominance of filamentous microorganisms. Moreover, respirometric analysis and modelling are highly informative in estimating the kinetics and stoichiometric parameters activated sludge which will enable to evaluate treatment performance (Insel et al., 2012).

2. Materials and Methods

Seed biomass were obtained from two different municipal wastewater treatment plants located in Marmara Region. Two lab scale SBRs were operated with a sludge age of 20 days at 22°C constant temperature room. The cultures were fed twice a day automatically with a synthetic solution characterizing domestic wastewater (ISO 8192) with a chemical oxygen demand (COD) of 400 mg/L. Reactors were stirred and aerated with constant air flow. Respirometric and microscopic analyses were conducted in order to determine the effect of seed biomass and its characteristics on the activated sludge structure as well as on the kinetic and stoichiometric coefficients. Oxygen uptake rate (OUR) measurements were performed with an Applitek Ra-COMBO respirometer. Modelling studies were conducted with modified Activated Sludge Model No. 1 (ASM1). The kinetic and stoichiometric parameters of the model were estimated using Aquasim 2.0 software.

3. Results

The SBRs inoculated from WWTP-1 and WWTP-2 were operated approximately for three months with an initial SS and VSS concentrations of 7050 and 4220 mg/L, 5180 and 3240 mg/L, respectively. The SBR-1 was deteriorated after 70 days of operation due to overgrowth of filamentous microorganisms which was not the case for SBR-2. The SVI values for SBR-1 and SBR-2 were 265 and 160 mL/g, respectively. The SS and VSS profiles
for both SBR-1 and SBR-2 are given in Figure 1. The micrographs in Figure 2 (a,b,c) clearly reflect the abundance of filamentous microorganisms in SBR-1, whereas after acclimation period the dominance of filamentous microorganisms decreased in SBR-2 Figure 2 (d,e,f). The effluent soluble COD in SBR-1 and SBR-2 were 70 and 40 mg/L, respectively. However, it should be underlined that the settling efficiency in the SBR-1 was very poor. Respirometric analyses were also evaluated to calculate total oxygen consumption. Both carbon removal and full nitrification was observed in two of the reactors based on the total oxygen consumption results (Figure 3).

![Figure 1](image1.png)

**Figure 1.** SS and VSS profiles in lab scale SBR reactors inoculated from WWTP-1 (a) and WWTP-2 (b).

![Figure 2](image2.png)

**Figure 2.** WWTP-1 seed biomass (Gram staining, 40x) (a), WWTP-1 acclimated sludge (wet mounting, 40x) (b), WWTP-1 acclimated sludge (Gram staining, 10x) (c), WWTP-2 seed biomass (Gram staining, 40x) (d), WWTP-2 acclimated sludge (Wet mounting, 20x) (e), WWTP-2 acclimated sludge (Gram staining, 40x) (f).

![Figure 3](image3.png)

**Figure 3.** OUR profiles observed in SBR-1 (a) and SBR-2 (b).

**References**


Synthesis and Characterisation of Silica gel 60 Supported Iron-Zinc Bimetallic Nanoparticles for the Adsorption of Malachite Green

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Keywords: Adsorption, bimetallic nanoparticles, iron-zinc, malachite green, silica gel 60

Abstract
In this study, silica gel 60 supported iron-zinc bimetallic nanoparticles (Si@Fe-ZnNPs) were synthesized by chemical co-precipitation method. The synthesized Si@Fe-ZnNPs were characterized by SEM, EDX, FTIR, and XRD analysis and they were tested for an adsorbent for removal of Malachite Green (MG) from aqueous solutions. Batch adsorption experiments were conducted using synthetic aqueous solutions of MG and the effects of the initial dye concentration, initial adsorbent concentration, and temperature were investigated. The equilibrium isotherms, kinetics, thermodynamics data and mass transfer effects of the adsorption process were evaluated to elucidate the adsorption mechanism of the dye molecules by the Si@Fe-ZnNPs.

1. Introduction
Adsorption process is still a widely used method for the removal of toxic pollutants from wastewaters because of its low cost, removal performance and ease of operation. Various combinations of iron-based bimetallic nanoparticles have been used as adsorbent for the elimination of hazardous contaminants such as dyestuffs, organic compounds and heavy metals and reports indicated that the pollutant adsorption rate by iron oxide nanoparticles was very slow. Moreover, incorporation of a second catalytic metal like such as Zn, Cu, Ni or Pd might enhance the adsorption rate compared with iron nanoparticles alone and also prevents oxidation in air [1]. In addition, loading bimetallic nanoparticle species onto solid supporters is a promising way due to loading improves the mechanical strength and removal efficiency of the adsorbent. Wide variety of organic, inorganic, and biological substances, such as silica gel, activated carbon, multiwalled carbon nanotube, zeolite, alginate, chitosan, gum, hydroxyapatite, could be used as solid supporters. In the present study, silica gel 60 supported Fe–Zn bimetallic nanoparticles (Si@Fe-ZnNPs) were synthesized, characterized, and used as an adsorbent to remove Malachite Green (MG) dye from aquatic media.

2. Materials and Methods
2.1. The synthesis of silica gel 60 supported Fe-Zn bimetallic nanoparticles
The synthesis of Fe-Zn bimetallic nanoparticles was carried out by chemical co-precipitation method. In the experiments, 25 mL of 0.4 M iron chloride and 25 mL of 0.2 M zinc chloride solution were mixed at room temperature for 15 min. Then 25 mL of 3.0 M sodium hydroxide solution was prepared and slowly added to the prepared salt solution. This mixture constantly stirred until the pH of 11 – 12 was reached. The changing of the colour of the salt solution from clear to intense black indicated the formation of Fe-ZnNPs. Then 0.5 g silica gel 60 was added to Fe-ZnNPs solution and the solution was stirred for 3 h at room temperature. The silica gel supported bimetallic nanoparticles were separated by centrifugation, washed with distilled water, and dried in an oven at 105°C for 12 h.
dried nanomaterials (Si@Fe-ZnNPs) were crushed to powder, stored in a glass bottle, and used for characterization and adsorption studies.

2.2. Adsorption Studies

The adsorption experiments were carried out in 250 mL Erlenmeyer flasks containing 100 mL of MG adsorption solution. 0.1 g of adsorbent, except for adsorbent concentration experiments, was contacted with 100 mL of MG solution at known initial dye concentration at natural pH of solutions. Then the flasks were agitated at a constant temperature and shaking rate. Samples were taken before mixing the Si@Fe-ZnNPs and dye solution and at pre-determined time intervals for the unadsorbed dye concentration in the solution. Samples were centrifuged and the supernatant liquid was analysed by UV-vis spectrophotometer at the wavelength of 618 nm.

3. Results

The SEM images showed that the spherical and nanosized (≈ 30 nm) particles were formed which were dispersed into the surface of silica gel 60. According to elemental analysis results, the elemental and quantitative weight composition (wt.%) of synthesized Si@Fe-ZnNPs was composed of 6.78 %Fe, 44.07 %Zn, 2.44 %Si, 8.56 %O and 42.38 %Cl elements. After adsorption, the detection of C and N elements in addition to Fe, Zn, Si, O and Cl elements, confirmed the adsorption of the dye molecules onto the Si@Fe-ZnNPs surface. According to the FT-IR spectrum of synthesized Si@Fe-ZnNPs, the adsorption bands at 584 cm\(^{-1}\) and 467 cm\(^{-1}\) refer to Fe-O stretches of \(\alpha\)-Fe\(_2\)O\(_3\) and metal-metal stretching vibration of \((\text{Zn}^{2+} - \text{O}^2-)\) in tetrahedral region that confirming the formation of Fe-ZnNPs. Moreover, the bands at 1067.8 and 490.96 cm\(^{-1}\) are attributed to Si-O-H, Si-O-Si and O-Si-O stretching and bending vibrations also confirmed that silica gel 60 was supported on the Fe-ZnNPs surface. The peaks at 20 = 34° and 45° correspond to ZnO and maghemite (\(\alpha\)-Fe\(_2\)O\(_3\)) structures in the XRD pattern of synthesized Si@Fe-ZnNPs and XRD diagram indicated that, the material was completely amorphous structure due to the change the crystallinity and phase after adsorption.

The optimum adsorption conditions were determined as natural pH 3.2 of solution, temperature 50°C, and adsorbent concentration 1.0 g/L. Also a linear increase was observed in equilibrium uptakes of MG when the initial dye concentrations were increased. The experimental equilibrium data were modelled with Langmuir and Freundlich isotherm models and it was found that, experimental equilibrium data could be well described by Langmuir isotherm model. The maximum monolayer coverage capacity of Si@Fe-ZnNPs for MG adsorption found to be 666.67 mg/g at optimum temperature. The pseudo-first order and the pseudo-second order kinetic models were applied to the experimental adsorption data and, it was concluded that the data were defined the best agreement with the pseudo-second order kinetic model. Weber Morris model was used to investigate the effect of mass transfer on the adsorption of MG onto Si@Fe-ZnNPs, it was observed that both the film (boundary layer) and intra-particle diffusion affected the studied adsorption process. The thermodynamic studies suggested that the adsorption process was endothermic, non-spontaneous and the positive \(\Delta S\) value indicated increased disorder at the solid-solution interface during the adsorption. Consequently, the synthesized Si@Fe-ZnNPs could show well adsorbent property for the removal of hazardous materials from wastewaters.

References

Treatment of Pharmaceutical Wastewater by Combination of Electro-Fenton, Electrocoagulation and Photocatalytic Oxidation Processes


Abstract

In this study, pharmaceutical industry wastewater that consisted of persistent pollutants was treated by combination of electro-Fenton (EcF), electrocoagulation (EC) and photocatalytic oxidation processes to remove total organic carbon (TOC) from wastewater. During EcF process, H₂O₂ amount was periodically added based on the calculated amount of released iron content from anode electro-dissolution. Then, EC and photocatalytic processes were further carried out to finalize the sequential treatment process, respectively. Optimum reaction times for these processes were initially investigated and then the ideal current density value was determined for EC process with iron plate electrodes. Finally, photocatalysis in UV/ZnO was applied to treat effluents from EC process.

Key Words: Pharmaceutical wastewater, electrocoagulation, electro-Fenton, photocatalytic oxidation, sequential systems

1. Introduction

Wastewaters generated in different pharmaceutical production operations, wherein several quantities of water are used for washing of solid cake, extraction, washing of equipment are generally discharged to nearby surrounding areas through drainage and river streams [Gadipelly et al., 2014]. In recent years, pharmaceuticals have also been considered as an emerging environmental problem due to their harmful effect on aquatic organisms, ecosystem and human’s life. Moreover, reuse of water after removal of pharmaceutical pollutants is required by industry because of the scarcity of water resources. Therefore, it is essential to progress treatment systems of pharmaceutical wastewaters as water management [Rivera-Utrilla et al., 2013]. However, pharmaceutical industry wastewater cannot be completely removed by single technology [Gadipelly et al., 2014]. In this study, pharmaceutical industry wastewater was treated by combination of EcF, EC and photocatalytic oxidation processes to remove TOC from wastewater.

2. Materials and Methods

The pharmaceutical industry wastewater used for experiments was provided from a company in Gebze, TURKEY. The wastewater was stored in a cold room (+4 ℃) to avoid any decomposition in wastewater quality. The wastewater characterization was performed according to Standard Methods [Rice et al., 2012]. H₂O₂ (35% w/w) were used as the oxidizing reagent and pH values were adjusted with H₂SO₄ and NaOH in the experiments. EcF and EC processes were implemented in the batch polypropylene (PP) electrochemical reactor with four electrodes made from iron and the working volume of the effluent was 0.5 L as shown in Fig. 1(a). Sequential photocatalytic oxidation process was than applied in the batch Pyrex column reactor as shown in Fig.1(b). EcF process was maintained in a pulsed current feeding by performing different periods of current on and off cycles. These cycles were repeated 10 times during the reaction time at pH 2. Necessary amount of H₂O₂ was added at the beginning of each current off cycles by adjusting the
amount in stoichiometric ratio (1:10) [Marco and Jose, 2006]. Prior to EC process, the pH was adjusted to the value of 7.5±0.3 to get effective coagulation process for 3 different current densities such as 5, 10 and 15 mA/cm². Finally, photocatalysis in UV/ZnO was applied to treat effluents from EC process.

3. Results

EcF process was initially performed in order to determine organic degradation in different time cycles. The degradation efficiency of EcF process was investigated by measuring TOC amounts of effluent samples. One of the important parameters for EC process is current density (CD) as it can be changed the metal hydroxide dosage ratio and also the bubble production rate, size and floc growth thus influencing the efficiency of the EC process [Sahu et al., 2015; Praveen et al., 2015]. The influence of current density on the TOC removal of EC process was investigated in this part of the study. Increase in TOC removal is usually expected by increasing the current density. As a third treatment step, UV/ZnO photocatalysis process was applied to treat effluents. The cost of electrode material and energy use were calculated based on the optimum experimental conditions of EcF, EC and photocatalytic oxidation. The well-known Faraday Law equation was used to calculate theoretical electrode consumption for EcF+EC processes [Scott, 1995; Rajeshwar et al., 1997]. At the end of these calculation total electrode and energy cost was calculated as per treated m³ wastewater. The results of this study showed that three-step sequential treatment process could be successfully treated persistent pollutants from pharmaceutical industry wastewater.

References

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**Study Total Synthesis Of Natural Anti-Marine Fouling Agent (Synthesis of 7th Intermediate Compound From Omaezallene Derivative)**

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**Keywords**: anti-marine fouling, omaezallene derivate, total synthesis

**Abstract**

Biofouling or Marine fouling was an unwanted phenomenon in marine transportation. Antifouling paints that contain a toxic substances have been used to limit damage caused by marine fouling organisms, for example TBT (tributyltin). That was very dangerous because TBT has hazaedous effect for marine environment and also became one of public health issues in present. One of solution come from Omaezallene compound which is isolated from red alga, Laurencia sp. The improvement of structure from Omaezallene and its derivatives was still needed for get optimum antifouling activities. Synthesis of 7th intermediate compound (5-Bromo-5-[3-(tert-butyl-dimethyl-silanyloxy)-tetrahydro-furan-2-y1]-4-trimethylsilanyloxy-pent-2-en-1-ol) 16a and 16b from omaezallene derivative without bromoallene group has been conducted. The results gave very important information for syhthesis of omaezallene derivative without bromoallene group in the future.

**1. Introduction**

The maintenance of ships, especially on their hull will gave some benefits. The ships will consume less fuel, travel smoothly and faster when their hulls are clean from fouling organisms, such as molluscs, barnacles, or algae (Anderson, 2002). There are two methods in the maintenance process, scraping the hull and coating the hull with modified coat which contain an antifouling agent e.g. TBT. The TBT can release to seawater and has negative effects such as toxicity to marine lives, persistence in the aquatic environment (Demirel *et al.*, 2013). Nevertheless, some research activities reported that TBT causes shell malformation of oysters (Alzieu *et al.*, 1986) and imposex of gastropod molluscs (Gibbs and Bryan, 1986).

In recent work, Umezawa *et al.* (2014) has screened marine algae for antifouling activity and discovered omaezallenes, which were extracted from a red alga, Laurencia sp. Herein, their group reports the isolation, structure elucidation, total synthesis, antifouling activity, and ecotoxicity of omaezallene and its congeners. Omaezallenes have two important functional groups are suspected of affecting on the antifouling properties, they are bromodiene and bromallene groups. However, the investigation of antifouling effects to omaezallene without bromallene group has not been conducted. In this research, the total synthesis study of omaezallene derivative has been done until 7th intermediate compound. The structure elucidation and synthesis method from this research also have been investigated and evaluated.
2. Materials and Methods

Materials

Chemicals used in this research were cis-2-butene-1,4-diol, 2,2,6,6-tetramethylpiperidine-1-oxyl free radical (TEMPO), iodobenzene diacetate, trimethylsilyl cyanide (TMS-CN) and tributylphosphine were purchased from TCI Trademark. Titanium tetraisopropoxide, sodium bis(2-methoxyethoxy)aluminum dihydride (Red-Al), imidazole, ethyl bromoacetate, toluene, triethylamine (Et₃N), N-bromosuccinimide (NBS), NaH (60% suspension in paraffin oil), tetra-n-butylammonium iodide, diisobutyl aluminum hydride (DIBAL), sodium bis(trimethylsilyl)amide (NaHMDS), hydrochloric acid (HCl), tetrahydrofuran (THF) super dehydrated, N,N-dimethyl formamide (DMF), were purchased from Kanto Chemical Cica Reagent. Chloroform-D₆ for NMR, HF-Pyridine complex, tert-butyldimethylsilyl chloride, 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ), 4-methoxybenzyl alcohol, tert-butyl hydroperoxide, and molecular sieves 4Å were purchased from Sigma Aldrich. L-(+)-diisopropyl tartrate, acetonitrile super dehydrated, phosphate pH standard 6.86 equimolal solution, Fe(OH)₂.7H₂O in 1 M solution and ethyl diethyl phosphonoacetate (EtO₂CCH₂P(O)(OEt)₂) were purchased from Wako.

Methods

\[
\text{HO} \quad \text{OH} \quad \text{PMBO} \quad \text{OH}
\]
cis-2-butene-1,4-diol

\[
\text{TMS-CN, Et₃N} \quad \text{CH₂Cl₂, rt, 30 min}
\]
1.) TMS-CN, Et₃N

\[
\text{O} \quad \text{O} \quad \text{TBSO}
\]
12.

\[
\text{EtO₂CCH₂P(O)(OEt)₂} \quad \text{NaHMDS, THF, -78 °C}
\]
1.) EtO₂CCH₂P(O)(OEt)₂

\[
\text{O} \quad \text{O} \quad \text{TBSO} \quad \text{H} \quad \text{Br}
\]
14.

\[
\text{R = OTMS} \quad \text{14a}
\]

\[
\text{R = OTMS} \quad \text{14b}
\]

3. Results

The product was obtained as colorless oil in 21% yield of 16a and 12% yield of 16b. Structure elucidation of the unsaturated alcohol 16a was performed by means of IR, ¹H-, ¹³C-NMR spectrometers and polarimeter ([α]₂₂⁰. [α]₁₀⁰ = -4.95 (c = 0.04, CHCl₃); IR (neat) 3451, 3011, 2930, 2857, 1470, 1253, 1052, 1096, 769 cm⁻¹, ¹H-NMR (400 MHz, CDCl₃), δ -0.02-0.03 (15H, s), 0.77-0.78 (9H, s), 1.12 (1H, br), 1.81-1.93 (2H, m), 3.74-3.82 (1H, q, \( J = 8.8 \) Hz), 3.85-3.89 (2H, t, \( J = 9.7 \) Hz), 3.92-3.94 (1H, t, \( J = 8 \) Hz), 4.04-4.05 (2H, d, \( J = 5.1 \) Hz), 4.32 (1H, s), δ 4.46 (1H, s), 5.61-5.64 (1H, m), 5.71-5.75 (1H, m), ¹³C-NMR (CDCl₃, 100 MHz) δ -4.9, -4.6, 0.0, 25.51, 25.54, 25.6, 35.4, 53.3, 56.5, 62.7, 66.9, 70.5, 72.3, 82.5, 129.9, 132.6.

Structure elucidation of the unsaturated alcohol 16b was performed by means of IR, ¹H-, ¹³C-NMR spectrometers and polarimeter ([α]₂₂⁰. [α]₁₀⁰ = -40.30 (c = 0.01, CHCl₃); IR (neat) 3451, 3011, 2930, 2857, 1470, 1253, 1052, 1096, 769 cm⁻¹, ¹H-NMR (400 MHz, CDCl₃), δ -0.06-0.01 (15H, s), 0.71-0.81 (9H, s), 1.10 (1H, br), 1.74-1.85 (2H, m), 3.56-3.60 (1H, q, \( J = 7.6 \) Hz), 3.79-3.79 (2H, t, \( J = 1.2 \) Hz), 3.90-3.91 (1H, t, \( J = 3.4 \) Hz), 4.02-4.04 (2H, d, \( J = 6.4 \) Hz), 4.28-4.29 (1H, t, \( J = 2.9 \) Hz), δ 4.42-4.43 (1H, t, \( J = 1.9 \) Hz), 5.69-5.70 (1H, m), 5.75-5.76 (1H, m), ¹³C-NMR (CDCl₃, 100 MHz) δ -5.0, -4.6, 0.0, 25.51, 25.54, 25.56, 35.1, 57.3, 62.8, 67.4, 71.6, 72.3, 83.3, 129.8, 131.3.
References

A Novel Potential Way for Polyethylene Reuse: Reduction of NiO via Polyethylene Pyrolysis

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Keywords: Polyethylene, Pyrolysis, Nickel oxide, Reuse, Metal oxide reduction, Thermodynamics

Abstract

This study introduces a novel potential way for polyethylene reuse. The method consists of simultaneous waste polyethylene pyrolysis and reduction of metal oxides by pyrolytic gas. NiO was chosen to demonstrate the feasibility of the method. Prior to the experiments, thermodynamic calculations were performed by a Gibbs’ free energy minimization method to predict gaseous species and solid phases likely to be present in the Ni-O-C-H-Ar system. The high density polyethylene (HDPE) pyrolysis and NiO reduction experiments were carried out simultaneously during heating to the temperatures in the range of 550-900 K. Mass measurement, X-ray diffraction (XRD), and scanning electron microscope techniques were used to characterize the products. It was determined that the high density polyethylene was pyrolyzed, and the extent of NiO reduction increased as the temperature increased to 900 K. XRD analysis indicated that NiO was completely reduced to Ni at 900 K. Based on the thermodynamic analysis, it was proposed that Ni was obtained as a result of the reactions between NiO and the pyrolytic gas species derived from HDPE pyrolysis process. The present study demonstrates that HDPE may be reused for the reduction, and carburization metal oxides.

1. Introduction

Waste materials have been usually discarded by landfilling method. This has the potential for soil and ground contamination. Pyrolysis method has received considerable attention for reuse/recycling of waste organic materials to reduce landfilling. It yields pyrolytic gas, oil and solid residues. These products have been utilized. For example, diesel oil has been produced from pyrolytic oil [Wong, 2015], and pyrolytic gas has been used as energy source. Metal oxides are conventionally reduced to metals by H₂ gas and solid carbon [Bouvier, 1985]. In the present study, waste polyethylene has been utilized as reducing agent precursor for metal oxide reduction. Specifically, NiO has been chosen to demonstrate the feasibility of the proposed method as Ni is an important element used in numerous alloys such as stainless steels, superalloys.

2. Materials and Methods

Waste high-density polyethylene (HDPE) and NiO powder were used as reactants. Two separate boats loaded with HDPE chunks and NiO powder were placed successively into the uniform temperature zone of a quartz tube. HDPE and NiO powder were heated simultaneously at a rate of 15 K/min to the target temperatures in the range of 550-900 K. Ar was allowed to flow at a rate of 42.5 scm to carry the gaseous species produced by HDPE pyrolysis to the NiO powder bed. After reaching the desired temperature, the reaction tube was cooled rapidly to the room temperature in Ar flow. The extent of HDPE pyrolysis and NiO reduction were determined by mass measurements using an electronic
balance. X-ray diffraction patterns from the Ni-containing powders were taken for phase analysis by a goniometer using copper Kα radiation with a wave length of 0.15418 nm. The morphology of the powders was examined by a scanning electron microscope.

3. Results

Fig. 1a shows the effect of heating temperature on the mass percentages of HDPE and NiO in Ar flow. The mass of HDPE appears to be essentially not affected by the temperature in the range 550 to 650 K as noticed from the plateau. At the higher temperatures, the mass decreases drastically to zero as the temperature increases to 900 K. This result indicates that the HDPE is completely pyrolyzed at 900 K. The NiO reduction seems to proceed in parallel to the HDPE pyrolysis as noticed from the figure. NiO reduction does not essentially occur in the temperature range of 550 to 650 K, where the HDPE pyrolysis is negligible. The mass, however, decreases as the temperature increases to 900 K. Fig. 1b shows the X-ray diffraction pattern of the product obtained at 750 K and 900 K. The pattern a exhibits NiO and Ni diffraction peaks, indicating that the NiO powder was partially reduced at 750 K. At the higher temperature of 900 K, the NiO reduction to Ni was completed as evidenced by the sole presence of Ni diffraction peaks in the pattern b.

![Graph showing mass percentage vs temperature for HDPE and NiO in Ar flow.]

**Figure 1.** (a) Variations of the mass with temperature for HDPE and NiO in Ar flow. (b) XRD patterns of the products obtained after heating NiO to 750 K and 900 K in Ar flow. Ni was obtained by the reaction between NiO particles and gaseous species derived from HDPE pyrolysis process. Thermodynamic calculations based on the Gibbs’ free energy minimization method predicts that pyrolytic gas consists of mainly CH₄, H₂ and higher hydrocarbons. Based on the calculations, some overall NiO reduction reactions may be suggested as

\[ \text{NiO} + \text{H}_2 \rightarrow \text{Ni} + \text{H}_2\text{O} \]
\[ \text{NiO} + \text{CH}_4 \rightarrow \text{Ni} + \text{CO} + 2\text{H}_2 \]

This study demonstrates that NiO could be reduced to Ni by the HDPE pyrolysis products. It is anticipated that the novel route presented here may be extended to the reduction and carburization of other materials, and will contribute to reuse/recycling of organic wastes in the near future.

References


Comparison of Ozonation, Adsorption and Air Stripping Process for Ammonia Nitrogen Removal From Real Textile Wastewater

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Keywords: Textile wastewater, ozonation, adsorption, air stripping process, NH4-N.

Abstract

In this study, the NH4-N, organic nitrogen, color and COD removal were investigated in raw wastewaters (WW1, WW2, WW3) and wastewater treatment plant discharge effluent (WW4) of a textile industry that performs cotton and polyester dyeing and printing processes. For this purpose, ozonation at low (pH 7.5) and high pH (pH 10), powder activated carbon adsorption and air stripping process at high pH (pH 10) were used. The maximum removal efficiency for NH4-N was obtained by ozonation (99%) at high pH conditions and by adsorption (95%) (for WW1, WW2 and WW3). However, the maximum removal efficiency for NH4-N obtained by the air stripping process was determined to be 56%. Due to the difficulty of chemical hydrolysis of the organic nitrogen, the removal efficiency by ozonation and air stripping process was low. The ozonation at high pH in the wastewater treatment effluent (WW4) was effective in NH4-N removal (84%).

As a result, ozonation of the raw wastewater at high pH values can be regarded as the most suitable method due to the high pH value of the industrial raw wastewater and economical and easy application according to other processes applied.

1. Introduction

Conventional methods such as activated sludge and chemical treatment systems are generally used for treatment of wastewater of textile industry. The application and design stages of conventional treatment methods generally take into account organic carbon removal. However, in the textile industry, which carries out the printing process and especially uses a large amount of urea, nitrogen removal may not be sufficient by existing conventional treatment methods (Öztürk ve Bal, 2015).

The Water Pollution Control Regulation are valid for the wastewater discharge limits in Turkey and the NH4-N discharge limit is 5 mg/L for the textile industry. Nitrogen in discharged wastewater can cause serious environmental problems such as algal blooms, fish deaths, decrease in oxygen level, decrease of biodiversity and decrease of aquatic plants and corals in receiving environments (Yunnen et al., 2016). This situation is also triggered by the increased production capacity and accordingly the increased consumption of dyestuffs and auxiliary chemicals.

In particular, in textile industry printing process wastewaters, generally it is not possible to reduce the concentration of high ammonia nitrogen to the discharge standards by conventional biological treatment methods. In this study, raw wastewater and biological wastewater treatment plant effluent of cotton and polyester printing and dyeing industry are treated by ozonation at low pH and high pH, activated carbon adsorption and air stripping.
process at high pH in laboratory scale and especially NH₄-N, organic nitrogen, color and COD removal efficiencies were determined and compared.

2. Materials and Methods

In the study, untreated textile wastewater (WW1, WW2 and WW3) taken at different times and biologically treated textile effluent (WW4) were used. NH₄-N, org-N, COD and color parameters were measured according to Standard Methods (APHA, 1998) in wastewater characterization and experimental study. The characterization of wastewater samples was given in Table 1.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Raw wastewater</th>
<th>Treated wastewater</th>
</tr>
</thead>
<tbody>
<tr>
<td>WW1</td>
<td>WW2</td>
<td>WW3</td>
</tr>
<tr>
<td>NH₄-N, mg/L</td>
<td>15,7</td>
<td>56,6</td>
</tr>
<tr>
<td>Org-N, mg/L</td>
<td>35,1</td>
<td>750,9</td>
</tr>
<tr>
<td>Color, Pt-Co</td>
<td>771</td>
<td>773</td>
</tr>
<tr>
<td>COD, mg/L</td>
<td>640</td>
<td>894</td>
</tr>
</tbody>
</table>

3. Results

As a result, ozonation of the raw wastewater at high pH values can be regarded as the most suitable method due to the high pH value of the industrial raw wastewater and economical and easy application according to other processes applied. However, in order to achieve NH₄-N removal under optimum conditions, it is appropriate to carry out more detailed and pilot scale studies in which cost analyzes are made.

![Figure 1. Comparison of NH₄-N removal efficiencies](image)

**References**


Madder Root as an Adsorbent for Chemical Oxygen Demand, Color and Aromaticity Removal of Natural and Synthetic Dyeing Effluents

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Keywords: Madder root, color removal, aromaticity, chemical oxygen demand, dyeing effluents.

Abstract

In this study, the use of madder root ash to remove chemical oxygen demand (COD), color and aromaticity (UV254 nm) of natural dyeing wastewater and synthetic dyeing wastewater were investigated. Natural dyeing wastewater is obtained by dyeing with madder root dye of woolen fabric. Synthetic dyeing wastewaters were obtained by dyeing with 1:1 metal complex dyes in order to obtain the same color which obtained after dyeing with madder root dye. Natural dyeing wastewater characteristics were as follows COD: 3402 mg/L, color: 237.2 m-1 and UV254 nm absorbance (aromaticity): 796.6 m-1. Synthetic dyeing wastewater characteristics were as follows COD: 8316 mg/L, color: 93.8 m-1 and UV254 nm absorbance: 231.1 m-1. In the study the effect of pH and adsorbent dosage on COD, color and aromaticity removals were investigated. According to the results the maximum COD, color and aromaticity removal rates for both natural and synthetic effluents obtained at pH 3. COD, color and aromaticity removal rates for natural dyeing wastewaters at pH 3 were as follows: 16%, 49% and 27%. For the synthetic dyeing effluents COD, color and aromaticity removal rates were 11%, 34% and 11% respectively. From the experimental results of optimum adsorbent dosages study the maximum COD, color and aromaticity removal rates for natural dyeing wastewaters obtained at 60 g/L of madder root ash dosages. At this dosages COD, color and aromaticity removal rates for natural dyeing wastewaters were as follows: 47%, 74% and 40%. For synthetic dyeing wastewater the maximum COD and color removal rates obtained as 25% and 74% respectively at madder root ash dosages of 60 g/L. Aromaticity removal rate of synthetic dyeing effluents reached to equilibrium at 10 g/L madder root ash dosages and obtained as 11%. It has been found that the madder root can be used as an adsorbent for COD, color and aromaticity removal of natural and synthetic dyeing effluents. It can be concluded that madder root is more efficient for treating its own dyeing wastewater than synthetic dyeing wastewaters.

1. Introduction

Natural dyes, obtained from plants, insects/animals and minerals, are renewable and sustainable bioresource products with minimum environmental impact and known since antiquity for their use in coloration of textiles (Shahid et al., 2013). Today, dyeing is a complex and specialized science. Nearly all dyes are now produced from synthetic compounds (Siva, 2007). Discharge of dye-bearing wastewater into natural streams and rivers from textile industries poses a severe problem, as dyes impart toxicity to aquatic life and are damaging the aesthetic nature of the environment (Srivastava and Rupainwar, 2011). Dye removal from coloured effluent is difficult because of its complex structure. Adsorption, a physical method, is considered to be an effective method for the removal of
dyes owing to its low maintenance, simple operation, and effectiveness (Sathiskumar et al., 2012, Wang, 2012).

In this study, we examined the possibility of using madder root firstly as a natural dye, then as a natural adsorbent for chemical oxygen demand (COD), color and aromaticity (UV254 nm) removal of its own (madder root) effluents and synthetic dyeing wastewater.

2. Materials and Methods

**Dyeing with madder root extract:** 100 ml of filtrated dye extract was used to provide the liquor ratio of 10:1 for 10 g. material. Dyeings were carried out at extract solution’s own pH value, which was 5.3.

**Adsorption studies:** The adsorption study was carried out with 50 mL of natural and synthetic dyeing wastewater samples. The pH of the 50 mL samples was adjusted to 3, 7 and 11 and 0.2 g of madder root ash were added. The prepared samples were then placed in a shaker and agitated at room temperature (25 °C) at 250 rpm for 150 min. After shaking, 10 mL samples were taken and centrifuged at 4000 rpm for 5 minutes to measure COD, color and UV254 nm absorbance (aromaticity). COD was determined according to standard methods (APHA, 2005).

3. Results

The highest COD, color and UV254 nm absorbance (aromaticity) removal efficiencies were obtained at pH 3 for natural and synthetic wastewater. The effect of the madder root ash on the COD removal rate is given in Figure 1. The efficiency of COD, color and aromaticity removal increases as the adsorbent doses increases. The maximum COD, color and aromaticity removal rates for natural dyeing wastewaters obtained at 60 g/L of madder root ash dosages. At this dosages COD, color and aromaticity removal rates for natural dyeing wastewaters were as follows: 47%, 74% and 40%. For synthetic dyeing wastewater the maximum COD and color removal rates obtained as 25% and 74% respectively at madder root ash dosages of 60 g/L.

![Figure 1](Image)

**Figure 1.** The effect of madder root ash doses on the COD, color and aromaticity removal efficiency

References


Green Synthesis of Pd/Fe Bimetallic Nanoparticles: Catalytic in situ Generation of \( \text{H}_2\text{O}_2 \) for Heterogeneous Fenton-like Degradation of Basic Red 46 and Direct Red 23

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Keywords: Palladium-iron bimetallic nanoparticles, Citrus limon, in situ \( \text{H}_2\text{O}_2 \), Heterogeneous Fenton-like reaction, catalyst, Basic Red 46, Direct Red 23

Abstract

In this study, Pd/Fe bimetallic nanoparticles (Pd/FeNPs) were biosynthesized by aqueous lemon (\textit{Citrus limon (L.) Burm. f.}) leaves extract as a reducing agent and were characterized by XRD, SEM, EDX and FTIR analyses. And then, Pd/FeNPs were utilized as a common heterogeneous catalyst for both in situ \( \text{H}_2\text{O}_2 \) synthesis by formic acid decomposition in the presence of oxygen and heterogeneous Fenton-like degradation of Basic Red 46 (BR 46) and Direct Red 23 (DR 23) azo dyes.

1. Introduction

In recent years, the wastewater treatment methods are called as Advanced Oxidation Processes (AOPs), including homogeneous Fenton reaction (\textit{Fe(II)/H}_2\text{O}_2), photo-Fenton reaction (\textit{Fe(II)/H}_2\text{O}_2/UV), ozonation (\textit{O}_3), wet peroxide ozonation (\textit{O}_3/\textit{H}_2\text{O}_2), \textit{H}_2\text{O}_2/UV, heterogeneous Fenton-like processes and photocatalytic (\textit{TiO}_2/UV and \textit{ZnO}/UV) processes have attracted considerable attention for the removal of toxic and carcinogenic organic/inorganic pollutants from water sources. Heterogeneous Fenton-like reaction is one of the popular advanced oxidation processes. Hydrogen peroxide (\textit{H}_2\text{O}_2) is the most preferred oxidizing agent because of its environmental friendliness, rapid and easy formation of hydroxyl radicals for degradation of contaminants in heterogeneous Fenton-like reactions. However, the problems such as, the use of hydrogen peroxide is much higher than which is converted into hydroxyl radicals during the reaction due to the hydrogen peroxide is fed to the system in bulk, the cost of commercial hydrogen peroxide is expensive, difficulties in synthesis method, danger of transport and storage, affect the process negatively. Therefore, the indirect synthesis of \( \text{H}_2\text{O}_2 \) catalytically in the reaction medium without adding \( \text{H}_2\text{O}_2 \) from the outside (in situ hydrogen peroxide synthesis) offers an advantage in avoiding problems caused by unnecessary use of \( \text{H}_2\text{O}_2 \) in the heterogeneous Fenton-like reactions. In this method which is called as in situ \( \text{H}_2\text{O}_2 \) synthesis; the catalytic decomposition of the organic compounds such as formic acid, hydrazine hydrate and hydroxyl amine etc., which have substituted hydrogen in their structure and mostly used for hydrogen production, leads to hydrogen gas generation and \( \text{H}_2\text{O}_2 \) can be synthesized by the reaction of hydrogen and oxygen added in reaction media [1, 2].

In this study, Pd/Fe bimetallic nanoparticles will be biosynthesized as a catalyst by aqueous lemon leaves extract as a reducing agent for both in situ \( \text{H}_2\text{O}_2 \) synthesis and the decolorisation of Basic Red 46 (BR 46) and Direct Red 23 (DR 23) azo dyes with heterogeneous Fenton-like reactions.

2. Materials and Methods

Green Synthesis of Pd/Fe Bimetallic Nanoparticles

The lemon leaves were firstly washed with distilled water and then air-dried at ambient temperature. For the preparation of extract, 10 g of dried leaves were boiled in 500
mL of distilled water in a beaker under continuously stirring for 60 min. For green synthesis of Pd/Fe NPs, 0.5 g of FeSO\(_4\)·7H\(_2\)O and 0.1 g of PdCl\(_2\) were dissolved in 60 mL aqueous extract of the lemon leaves at 60 ºC under vigorous stirring. Then, a solution of 1.0 M Na\(_2\)CO\(_3\) was added dropwise to the mixture to obtain alkaline pH while changing the color to dark brown. After being stirred again for 3 hours at the same temperature, a suspension was formed which gave precipitate of Pd/FeNPs on centrifugation at 4000 rpm and the obtained nanoparticles were washed with distilled water, respectively, and then dried at 105ºC in an oven.

**Heterogeneous Fenton like decolourisation experiments with in-situ-generated H\(_2\)O\(_2\)**

In-situ generation of hydrogen peroxide was performed by formic acid decomposition and O\(_2\). Heterogeneous Fenton like decolourisation experiments with in situ H\(_2\)O\(_2\) generation were carried out in a 250 mL magnetically stirred three-necked glass balloon. 50 mL of 20 mg/L BR 46 (or DR 23) and 50 mL of 500 mM formic acid were contacted with 1 g/L of catalyst. Initial pH of dye solutions was adjusted to 3.0 by 0.1 N HCl or 0.1 N NaOH solutions. Oxygen/air was passed into the reaction medium with a compressor. Dye concentrations were monitored by sampling at regular time intervals and analyzed by using the UV–vis spectrophotometer at the wavelength of 530 and 507 nm for BR 46 and DR 23, respectively. To further verify the in-situ generated H\(_2\)O\(_2\), the solution (deionized water instead of dye) during the reaction was filtrated and monitored by spectrophotometric determination using titanium sulfate at 400 nm.

### 3. Results

The crystalline structure of Pd/FeNPs was confirmed with XRD measurements. According to XRD analysis results, the presence of palladium and iron was confirmed in the structure of Pd/FeNPs. In order to identify the structure of catalyst in detail; SEM, EDX and FT-IR analysis will be also carried out. In this study, in situ H\(_2\)O\(_2\) generation was carried out by formic acid decomposition and the formation of H\(_2\)O\(_2\) was proved by the UV-vis absorbance spectrum of the resulting yellow complex between H\(_2\)O\(_2\) and titanium sulfate at 400 nm. In the heterogeneous Fenton like decolourisation studies with in situ H\(_2\)O\(_2\) generation, the decolourisation percentages ≈ 95% for BR 46 and ≈93% for DR 23 were obtained at the conditions of 20 mg/L of initial dye concentration, pH 3.0, 1 g/L of catalyst concentration, 25ºC ambient temperature and 500 mM- 50 mL of HCOOH concentration. It was determined that Fe and Pd played important roles in the synergistic effect, that is, Pd nanoparticles worked in in situ H\(_2\)O\(_2\) generation by formic acid decomposition and Fe nanoparticles worked in decompose H\(_2\)O\(_2\) for generating \(\cdot\)OH radicals to decolourisation of BR 46 and DR 23. Moreover, the adsorbent property of Pd/FeNPs was investigated in the same experimental conditions but the absence of formic acid and H\(_2\)O\(_2\). These control experiments showed that, almost no colour removal percentages were found both two dyes. In order to determine the decolourisation efficiency of heterogeneous Fenton-like reaction which was carried out by in situ H\(_2\)O\(_2\) synthesis, the effects of reaction parameters such as, the concentration of formic acid, initial pH of dye solutions, initial dye concentrations and catalyst concentration will be also investigated experimentally in detail. Consequently, the synthesized catalyst displayed excellent performances for BR 46 and DR 23 removal by in-situ generation of hydrogen peroxide and heterogeneous Fenton-like catalytic reaction.

### References


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\textbf{Keywords}: Aeration, EAPR-aeration, Lead (Pb), Phyto-aeration, Phytoremediation, Water lettuce

\textbf{Abstract}

This study was aimed to enhance of phytoremediation on the removal of Pb in the wastewater using electro-assisted and aeration system here in after referred as EAPR-aeration and up-take by water lettuce (*Pistia stratiotes* L.) as accumulator plant. A constant DC of 2V and air flow rate of 5 L/min in 15 L wastewater was applied. The effectiveness of EAPR-aeration system, phyto-aeration and phytoremediation on the wastewater treatment was compared. Plant appearance was also monitored by the measurement of chlorophyll content using UV-Vis Spectroscopy after the acetone extraction and heavy metal concentration was measured by Flame-Atomic Absorption Spectroscopy (Flame-AAS). The results showed that the decreasing of Pb concentration in the wastewater as much as 87.3%, higher than that phyto-aeration (57.5%) and phytoremediation (30%). The absorption of Pb by water lettuce on the basis of EAPR-aeration process was much lower than that in the phytoremediation and phytoremediation-aeration. The concentration of chlorophyll appears to be higher in phytoremediation method, because in this method the plant absorbs the metal naturally, whereas in the EAPR-aeration the chlorophyll concentration is lower due to the aeration and electro-assisted system which makes the plant more absorb metal than other methods.

1. Introduction

Water from mining or industrial activity and domestic wastewater such as college laboratory waste are included in the group of hazardous and toxic materials. Phytoremediation is a technique of utilizing plants in lowering contaminants such as heavy metals in soil or water (Astuti, 2004). However, the phytoremediation process also has several disadvantages, including short plant roots, slow biomass growth, and susceptible to toxicity (Hodko et al, 2000). The combined technology of electrokinetic process with phytoremediation called Electro-Assisted Phytoremediation (EAPR) (Putra et al., 2013, Cang et al., 2011) may be used as an alternative to overcome the deficiency in phytoremediation process. In this study, the wastewater treatment by a combine of EAPR and aeration system were assesseed by using water lettuce (*Pistia stratiotes* L.) as an accumulators plant of heavy metal in wastewater. In addition, stress conditions occurred in plants were observed by measuring the concentrate of chlorophyll and observing phytomorphology changing.
2. Materials and Methods

All experiments were running in three sets of reactor namely phytoremediation, phytoremediation-aeration and EAPR-aeration reactor with dimensions of 40cm (l) × 20cm (w) × 25cm (h) to accommodate 15 L of Hoagland solution which already contaminated by 100 mg/L of Pb prepared from Pb(NO₃)₂ salts and containing three water lettuce (Pistia stratiotes L.) in each reactor. The plants were grown in a light/dark cycle for 12/12 h. controlled by an intra-matrix timer. In the phytoremediation-aeration and EAPR-aeration reactor, it was equipped with four air diffuser with an air flow rate of 5 L/mins. In addition, the EAPR-aeration system was assisted by a DC constant voltage of 2V. The stainless steel cathode (negative) electrode in this system was a designed mesh-shaped pot (see Fig 1.), and four titanium rod anode (positive) electrodes were placed at each reactor angle.

3. Results

The effectiveness of EAPR-aeration system was evaluated by taken water samples from the reactor once every 24 h at three level points as shown in Fig 1. The combination of the EAPR system, which was then supplemented by oxygen through an aeration system, was used to improve the EAPR's ability to overcome the effect of faster exposure of plant toxicity than a normal process due to metal ions much concentrated around the plant root affected by a special designed cathode-pot electrode. Compared with EAPR-aeration system, the decreasing rate of lead concentration from the bottom, middle and top points were quiet low subsequently from contaminated water in the phytoremediation and phyto-aeration system. For example, the process could reduce 30.6% (62.2 mg/L), 57.6% (35.3 mg/L) and 88.2% (10.3 mg/L) from initial lead concentration respectively for phytoremediation, phyto-aeration and EAPR-aeration system in the 5 d remediation process. This results suggesting that the accumulative rate concentration was enhanced faster by electro-assisted in the EAPR-aeration system than other systems.

![Figure 1](image.png)

Figure 1. Designed EAPR-aeration reactor (a), designed cathode-pot electrode with sampling points level in the reactor (b) and profiles of decreasing lead (Pb) concentration in each treatment (c).

References

Phosphorus removal from sludge centrant liquor by a packed-bed electrocoagulation reactor using iron scrap anodes

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Abstract

Phosphorus (P) was removed from sludge centrant liquor by batch and continuous packed-bed electrocoagulation (PBEC) reactors using iron (Fe) scrap anodes. The influence of parameters such as initial pH (4 - 8.12), applied current (i = 0.05 - 0.3 A), inlet flow rate (Qw = 5 - 30 mL/min), amount of scrap anodes (m_scrap = 30.23 - 60.49 g) and air flow rate (Q_air = 0 - 5 mL/min) on P removal from the centrate effluent were analysed. The optimums to achieve > 99.5% P removals (C_f = ≤ 0.25 mg P/L) for batch operations were: pH_i = 8.12, i = 0.20 A, Q_air = 5 mL/min, m_scrap = 30.23 g and EC time ≥ 70 min. The operating cost, amount of sludge, energy and electrode consumptions at these optimums were; 0.364 $/m³, 1.103 kg/m³, 1.021 kWh/m³ and 0.366 kg/m³ respectively. In addition, the removed phosphorus per electrochemically generated Fe dosage (q_t) and removal mole ratio were calculated as q_t = 127.8 mg P/g Fe (or 0.0418 mg P/Coulomb) and n_Fe/P = 3.26 mole/mole, respectively. For the continuous flow operation, optimum conditions to achieve > 99.5% P removal was pH_i = 8.12, i = 0.20 A, Q_air = 5 L/min, EC time = 140 min (retention time in the reactor = 25 min), Q_w = 30 mL/min and m_scrap = 30.23 g. The operating cost, energy and electrode consumptions, amount of sludge, for the continuous PBEC were 0.143 $/m³, 0.513 kWh/m³, 0.116 kg/m³, 0.283 kg/m³, n_Fe/P = 5.76 mole/mole and q_t = 394.8 mg P/g Fe (or 0.117 mg P/C). The results show that batch and continuous EC processes using Fe scrap anodes are effective for P removal from sludge centrant liquor of a municipal wastewater treatment plant.

1. Introduction

Anaerobic digestion of sludge from municipal wastewater treatment plants produces biogas and stabilized biomass. The centrifugal dewatering of digested biomass produces dewatered sludge cake in addition to a liquid fraction (centrate liquor). The centrate is rich in nutrient such as ammonia, orthophosphate and organic loadings, which may cause eutrophication if discharged to receiving surface water bodies (Metcalf and Eddy, 2003). The centrate is usually returned to the starting stage of treatment plant for reprocessing, leading to the gradual build-up of phosphorus in the plant and decreasing phosphorus treatment efficiency (Fux et al., 2002). In this regard, phosphate removal from wastewater has been studies with different techniques like chemical precipitation, electrocoagulation, adsorption, ion-exchange, and membrane processes (Ramasahayam et al., 2014). Compared to the other processes, EC is effective, easy to operate, time saving, reduction in chemical addition and less sludge production, among others (Lacasa et al., 2011). In EC process, electrochemical dissolution of anode generates the coagulants, as H2 gas is generated simultaneously at the cathode. The utilization of waste scraps from metal machining and metalworking shops as anodes is advantageous both in terms of cost effectiveness and environmental point of view. The scrap anodes also have a larger contact surface area than the other shape of the anodes, thereby providing more contact area between the electrodes and pollutants in the EC reactor,
hence, increasing process efficiency. Published literature on phosphorus removal sing Fe or Al scrap anodes is very limited.

2. Materials and Methods

The sludge centrate liquor was obtained from Istanbul municipal wastewater treatment plant. The characterization of centrate is: pH = 8.12, conductivity = 315 ms/cm, $C_i = 47.05$ mg PO$_4$-P/L, COD = 130 mg/L and total Kjeldahl nitrogen = 128.5 mg/L. A perforated cylindrically titanium cathode inserted in a 500 ml cylindrical packed-bed EC reactor was used. The Fe scrap packed-bed anode was centrally inserted in the cathode. An air-fed diffuser was attached underneath the reactor and air was continuously supplied to ensure mixing. The centrate liquor (750 mL) was placed in the EC reactor and the system was connected to DC power supply. Samples were collected from the reactor at designated time intervals for analyses by Vanadomolybdate phosphoric acid Methods (APHA, 1998).

3. Results

For applied current of 0.05, 0.1, 0.2 and 0.3 A at pH$_i$ = 8.12 and $C_i = 47.05$ mg/L. Fig.1(a) illustrates the residual P concentration. EC time for > 99% P removal was > 90, > 90, 60 and 30 min, respectively, for this current values. Meanwhile, operating costs to achieve > 99% P removal at applied current of 0.05, 0.1, 0.0 and 0.3 A were 0.114, 0.215, 0.335 and 0.342 $/m^3$, respectively. The calculated phosphorous removal capacity at this current vaules varied from 147 – 378.7 mg P/g Fe as shown in Fig.1(b).

![Figure 1](image)

Removal efficiency of phosphate ions decreased with increasing initial pH$_i$. The time required to obtain > 99% phosphate removals doubled from 40 min to 90 min as pH$_i$ varried from 4 - 8.12. The effluent pH$_f$ of the EC process ranged from 7.36 to 8.55. The increase of solution pH during EC treatment is associated to the formation of hydrogen gas and hydroxyl ions. Phosphate removal efficiency decreased as the inlet flow rate was increased. Consequently, the time required to obtain > 99% phosphate removals raised from 70 min at 5 ml/min to 110 min at 30 ml/min. However, on economic point of view, treatment at high flow rates was more economically viable.

References


Phosphorus Release and Nutrient Recovery from Waste Activated Sludge Through Mesophilic Alkaline Fermentation

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Keywords: Mesophilic, alkaline, fermentation, nutrient, recovery, struvite.

1. Introduction

Uncontrolled struvite formation (magnesium ammonium phosphate) has been a big issue in wastewater treatment plants, most commonly in anaerobic digesters or downstream dewatering facilities. Besides, the use of struvite in agriculture as a slow release phosphorus fertilizer is a promising alternative for sustainable management of phosphorus especially while considering the phosphorus depletion. To achieve efficient struvite precipitation prior to anaerobic digestion, it is a necessity to release nutrients from bacterial cells as initial step. This paper represents the mesophilic alkaline fermentation studies for the nutrient recovery from excess sludge.

2. Materials and Methods

Fermentation

Sludge and dewatering reject waters were obtained from Atakoy Enhanced Biological Wastewater Treatment Plant. To achieve sludge solubilization, therefore nutrient release, low mesophilic (ambient temperature) and mesophilic (30°C) alkaline fermentation studies were run at different pH levels as 8, 9 and 10. Sludge samples were collected periodically, and TP, PO₄³⁻, NH₄, COD, MLSS and MLVSS were determined on Standard Methods (APHA, 20th edition). COD and PO₄-P releases were determined according to Equation 1. Volatile fatty acids (VFA) were measured by Shimadzu GC-2014. Statistical analyzes were applied by PSPP with Mann Whitney U test.

\[
\text{Release(%)=} \left( \frac{\text{soluble COD,P-soluble COD,P initial}}{\text{particulate COD,P initial}} \right) \times 100
\]

MAP Production

Dewatering reject waters were mixed with supernatants of fermented sludges and this liquor was processed in a lab-scale struvite precipitation system. pH of the liquor was adjusted as 8.5 by a pH control system with NaOH supplement or by an air pump with CO₂ stripping and monitored continuously by a pH sensor. After precipitation, precipitates were collected and will be analysed with X-ray Diffraction (XRD).

3. Results

Long-term fermentation studies between 5 and 23 days was performed to determine the optimum conditions for nutrient release. As shown in Figure 1.1, mesophilic fermentation
at pH:10 showed the highest phosphorus release. Higher temperature slightly enhanced the phosphorus release also in pH:9 and pH:8 experiments without any significant differences (p:0.121 and p:0.275), thus low mesophilic temperature might be more advantageous due to energy cost for heating. Also, losses in orthophosphate concentration were appeared after a while, especially in low mesophilic conditions possibly due to phosphorus precipitation. Therefore, short fermentation periods even as one day might be another cost saving and effective option. Besides phosphorus, up to 1000% increase in ammonia concentration was observed during fermentation studies.

Highest COD release was also observed in mesophilic pH:10 experiments. Furthermore, VFA production was greater in pH:10 fermentation than pH:8 at 30°C (Figure 2.2) in line with the study of Chen et al. (2007) which proposes the alkaline pH enhances VFA production by increasing hydrolysis rate so that soluble substrates for acidification and inhibiting the activity of methanogens.

References
Preparation and Characterization of PDMS/SiO$_2$ Mixed Matrix Membranes for Separation of Bio-alcohols from Fermentation Broths

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Keywords: Pervaporation, Membrane, Polydimethylsiloxane, Bio-alcohol, Fermentation

Abstract

The pervaporation separation method is considered to be a promising technique for bio-alcohol recovery from fermentation broths. In this study, poly(dimethylsiloxane) (PDMS) and PDMS/SiO$_2$ mixed matrix membranes were prepared with a novel preparation method. PDMS and PDMS/SiO$_2$ membranes were characterized by scanning electron microscopy (SEM), Fourier-transform infrared (FTIR), thermal gravimetric analysis (TGA) and dynamic mechanical analysis (DMA). Sorption and permeation studies were performed at 30, 40, 50°C for butanol, ethanol and water. Experimental results showed that the nanoparticle incorporation into the polymeric matrix enhanced the membrane performance, and the prepared membranes can be used for bio-alcohol separation.

1. Introduction

In general, separation methods used for the separation and purification of bio-alcohol are the distillation, adsorption, extraction, pervaporation, reverse osmosis or "gas stripping" methods (Oudshoorn et al., 2009) As energy issues have become increasingly important, there has been a growing interest towards separation processes with low energy consumption (Kuhn et al., 2009). Pervaporation (PV) has a potential to efficiently recover biofuels from fermentation broths (Vane, 2005).

There has been an increasing attention for alcohol-permselectivity pervaporation in bio-alcohol production due to the advantages of environmental friendliness and low energy consumption (Zhao and Jin, 2017). In the pervaporation process, the feed mixture is maintained in contact with one side of a nonporous membrane. Feed components leave the membrane as a vapour by vacuum application. The driving force for the transport is a difference in the partial vapor pressure of the component between the feed and permeate sides of the membrane. The membrane material used is a hydrophobic polymer since transportation of organic components from the fermentation broth is preferred (Kaminski et al., 2011).

2. Materials and Methods

Two-component PDMS elastomer was purchased from GE Silicones. We used a 10:1 (by weight) mixture of PDMS base/curing agent(RTV 655 A/B). Chloroform, ethanol and butanol were obtained from Merck. Ethyl acetate and the silicon dioxide (SiO$_2$)
nanoparticles coated with silane were purchased from VWR Chemicals and Nanografi Nano Technology, respectively. Nanoparticles (NP) were dispersed into the chloroform in an ultrasonic water bath for 1h. After the ultrasonic treatment, the curing agent (B) was added and mixed at mechanical stirrer for 2h. Viscous PDMS (A) was diluted in chloroform with a mechanical stirrer for 1h. Then PDMS (A) to NP/B mixture was added. They were all mixed together for 1h. The mixture (A/B/NP) was held under vacuum for 2h to remove the air bubbles. The mixture was poured onto glass Petri dishes. Then, the membranes were cured at 65°C for 4h.

3. Results

The sorption behavior of homogeneous and nanoparticle-filled PDMS membranes in pure butanol, ethanol and water at different temperatures was given in Figure 1.

Sorption results indicate that the sorption amount increases with the increasing of temperature for both cases as the polymer chain mobility increases. The sorption percentages of butanol and ethanol are evidently higher than water sorption due to chemical affinity between PDMS and alcohols. Also, it is clear that both homogeneous and filled PDMS membranes preferentially sorb butanol, and the amounts of butanol sorption in SiO2-filled membrane are higher than the sorption values obtained in homogeneous PDMS membrane at all temperatures. As a result, the nanosized SiO2-filled PDMS membrane prepared can be used effectively for bio-alcohol recovery by pervaporation method.

References

Nitrogen and Phosphorus Recovery from the Liquid Fraction of Anaerobic Digestate

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Keywords: Liquid fraction of digestate, Nitrogen, Phosphorus, nutrient recovery, chicken manure

Abstract
Biogas plant digestates are rich in nutrients such as nitrogen (N), phosphorous (P), and potassium. Nutrient recovery from digestate is a promising approach; however, more research is needed to make it efficient and economically feasible. This study aims to optimize phosphorus and nitrogen recovery from the Liquid Fraction of Digestate of chicken manure (CM-LFD). Headspace flushing (HSF) and struvite precipitation experiments were conducted to recover N and P, respectively. HSF reduced ammonium concentration from 5390 mg/L to 2180 mg/L. Phosphate removal of 86.5% was achieved by struvite precipitation. Our results show that molar ratio of 0.9:1 (Mg: P) with no pH adjustment will be appropriate for the forthcoming struvite precipitation experiments using a fluidized bed reactor.

1. Introduction
Recently there is a worldwide rapid growing of poultry and livestock industries, which has led to large quantities of animal waste to be produced. Gungor-Demirci and Demirer (2004) stated that the production of cattle and poultry manure in Turkey was approximately 20 million tons of dry matter in 2000.

Anaerobic digestion is an established process to convert organic waste to a more stable form with the advantage of biogas production. The resulted low carbon digestate can be directly applied to soil as an alternative source of fertilizer. However, that might result in serious environmental problems because of the high nutrient load. Therefore, treatment of digestate is necessary to reduce its negative impact on the environment.

From another point of view, digestate (mainly LFD) can be recognized as a mine for fertilizer recovery. Full scale application of ammonia stripping has been investigated (Bolzonella et al., 2017). Struvite precipitation is mainly limited to industrial and wastewater slurries, however, research is ongoing to apply this technique for digestate (Lebuf et al., 2013). This study aims to optimize P and N recovery from CM-LFD.

2. Materials and Methods

Head space flushing
In each HSF experiment air stream was applied onto a vigorously mixed CM digestate (in bottles filled with 1000 mL of digestate) to remove the free ammonia with convection according to the two-film theory. Air was not directly given to the digestate; it was passed over it. Here, air reduced the boundary layer thickness on the digestate surface with removing NH₃ and also CO₂. Removal of CO₂ increased the pH, which boosted NH₃ removal. The digestate bottle was connected to an acid (H₂SO₄) containing bottle, where the stripped ammonia was collected as ammonium sulfate ((NH₄)₂SO₄).
Struvite precipitation

Struvite precipitation was conducted with the main purpose of phosphorus removal. Several batch scale experiments were conducted in 100 mL bottles containing 40 mL of CM-LFD. Magnesium is deficient in cow manure; therefore an external source of magnesium as MgSO₄·7H₂O was added to initiate the precipitation process. Bottles were placed on an orbital shaker and mixed for 10 min firstly at 200 rpm and then at 100 rpm. The total shaking period was one hour. Experiments were conducted at 25 °C. Struvite precipitation was optimized according to different operational parameters. The parameters tested were:

- Molar ratio: Molar ratios of 1:0.5, 1:0.7, 1:0.9, 1:1, 1:1.1, and 1:1.5 of Mg²⁺:P were tested.
- pH: Struvite precipitation was conducted at different values of pH: 9.5, 10 and 10.5.
- The mode of magnesium addition: Instead of adding the whole amount of Mg²⁺ at once, the same amount of Mg²⁺ was added at smaller doses at regular intervals throughout the experiment.

3. Results

HSF reduced the ammonium concentration of the CM-LFD from 5390 mg/L to 2180 mg/L (Figure 1). This digestate with reduced ammonium concentration was used for our subsequent struvite precipitation experiments. Our results showed that phosphorus recovery of 86.5% could be achieved at molar ratio of 0.9:1, however no significant improvement was recognized at higher molar ratios (Figure 2). No effect was observed for higher pH levels or intermittent magnesium additions. Therefore, it is concluded that a molar ratio of 0.9:1 will be appropriate for the forthcoming struvite precipitation experiments which will be conducted in a fluidized bed reactor.

References


Potential Permeable Reactive Barrier Materials for the Treatment of Landfill Leachate

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Keywords: landfill leachate, residues, potential reactive materials, permeable reactive barriers

Abstract

Alternative reactive materials and treatment methods for leachate and/or leachate contaminated ground water are under continuous research. Besides preventing or reducing waste production, the Waste Framework Directive (WFD) (Directive 2008/98/EC) asks member states to take appropriate measures to increase the recovery of waste by means of recycling, reuse or reclamation or any other process with a view to extracting secondary raw materials. In this study, natural materials, residues or wastes such as volcanic slag (VS), blast furnace slag (BFS), organic compost (OC), pumice (PU), sepiolite (SE) and activated carbon (AC) were tested as potential reactive materials for further use in permeable reactive barriers (PRBs). The leachate used in the study was obtained from Samsun Municipal Solid Waste Sanitary Landfill. Analyses conducted on leachate revealed average concentrations of chemical oxygen demand (COD), ammonium, sulfate, phosphate, and nitrate as 10,773 mg O₂/L, 1669 mg/L, 583 mg/L, 14,2 mg/L and 7,9 mg/L, respectively. Lab-scale tests comprised of batch and column tests. Initial batch test performed were leaching tests followed by kinetic tests. Results showed different chemical leaching potentials for each reactive material. VS presented high ammonium, PU high chloride and SE heavy metal leaching at different levels. Kinetic tests on the other hand reflected that VS, PU, SE and AC are capable in removing various constituents from landfill leachate, reaching 75% COD and 100% PO₄.

1. Introduction

The management of landfill leachate continues to be an important task, requiring monitoring and maintenance of the collection and treatment system. Landfill leachate is a highly concentrated wastewater with a wide variety of contaminants containing organic and inorganic compounds, heavy metals etc. Leachate leaching into the ground generally happens in older landfills without proper liner and drainage system. Leachate seeping from a landfill may finally pollute the groundwater beneath the landfill, further causing to environmental risks. The transport of leachate plume can be controlled by a permeable reactive barrier (PRB). PRB are among the low cost and low energy remediation approaches. PRBs simply comprise of treatment zones containing reactive materials capable of transforming contaminants in a plume into less harmful or immobile species. Within the scope of this study, natural materials, residues or wastes such as volcanic slag (VS), blast furnace slag (BFS), organic compost (OC), pumice (PU), sepiolite (SE) and activated carbon (AC) as potential reactive materials for PRBs. Experiments carried out were lab-scale comprising of batch and column tests.
2. Materials and Methods

All reactive materials were air-dried and sieved below 2 mm particle size. In order to determine the leaching potential of constituents from the reactive materials leaching tests were performed. Batch experiments were conducted by treating leachate with reactive materials under identical experimental conditions of the leaching tests. Experiments continued for 96 hours at room temperature. In the column experiments PVC columns with 52.5 cm length and 4 cm internal diameter were used. Each column was filled with one reactive material that was found effective by batch tests results. The flow rate of columns was chosen to be 60 mL d\(^{-1}\). All samples were first centrifuged then filtered using 0.45 µm MF-Millipore MCE Membrane syringe filters before analyses. Ions in solutions (\(\text{SO}_4^{2-}\), \(\text{F}^-\), \(\text{Cl}^-\), \(\text{NO}_3^-\) and \(\text{NH}_4^+\)) were measured by Dionex ICS-5000 ion chromatography system. pH was measured with Sartorius PB 20 pH meter. Heavy metals analyses were made with UNICOM 929 AAS flame atomic adsorption spectrometer (APHA/AWWA/WPCF, 1998). The chemical oxygen demand (COD) was determined according to the closed reflux method (APHA/AWFA/WPCF, 1998).

3. Results

Within this study, batch tests were carried out as leaching and kinetic tests. Leaching tests aimed to check the reactives capacity to release chemicals into solution. All reactives represent different capabilities in releasing chemicals. VS presented high ammonium, PU high chloride and SE heavy metal leaching at different levels. Kinetic tests helped to determine the ability of reactive materials to remove several chemical compounds from landfill leachate. These experiments demonstrated that activated carbon removed Ni\(^{2+}\) and Zn\(^{2+}\) approximately 100%. High removal levels were also observed for COD (<70%) as shown in Figure 1. Ammonium removal was not over 30% for activated carbon. However, increased concentrations of chloride, fluoride, sulfate, measured in the solution were attributed to their release from reactive material which was confirmed by the leaching tests. Pumice was also able to remove several parameters from leachate such as COD, nitrate and zinc. Efficiencies determined were 65% for COD, 27% for Zn\(^{2+}\) and 22% for NH\(_4^+\) (Figure 2). On the contrary, Ni\(^{2+}\) was not removed by pumice. Sulfate, fluoride and chloride release was similarly observed for PU. Likewise it was observed that volcanic slag has tendency to retain COD and nitrate at high degrees. Considering the results of column tests activated carbon was the most effective material generally to remove most parameters (heavy metals and COD) as expressed in Figure 3. Activated carbon had the highest removal efficiencies of COD, ammonium and heavy metals (Cd\(^{2+}\), Cu\(^{2+}\), Ni\(^{2+}\), Zn\(^{2+}\)) as was similarly observed for the batch experiments. Sepiolite also seems to have the capability to remove heavy metals (Cd\(^{2+}\), Cu\(^{2+}\), Ni\(^{2+}\), Zn\(^{2+}\)) at high degrees (>90%) and a similar trend of ammonium, was represented in the sepiolite column. Conversely for COD removal sepiolite column was early exhausted.

References

Preliminary Results for Start-up and Adaptation of an EGSB Reactor for Valorization and Treatment of Source Separated Human Urine

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Keywords: Source separated human urine, Anaerobic processing/Expanded granular sludge bed (EGSB) reactor, salinity, adaptation/start up, COD removal/Biogas production, Resource recovery.

Abstract.

Processing of the liquid phase during nutrient recovery from source separated urine is an important issue and anaerobic treatment is considered in this work as an option. Adaptation of an anaerobic biomass for urine which has high nutrient and COD content and salinity was observed for over two months. 75% and 60% of removal could be achieved for soluble and total COD respectively with minor amounts of NH4+ release. The amount of CH4 produced was calculated from COD removal as 0.35 l CH4/g COD and 0.24 l CH4/l urine.

1. Introduction

One of the most effective ways of recycling nutrients in domestic wastewater is segregation of human urine at the source and processing it further to produce fertilizers to be returned to the food chain. Human urine is a nutrient rich stream with over 80% nitrogen, and 50% phosphorus and potassium in domestic wastewater in addition to highly concentrated organic matter content, and high salinity (Beler-Baykal, 2015). Ion exchange/adsorption is one of the successful methods of recovering nutrients from urine which may be recycled to agricultural use (Beler-Baykal et al, 2004, 2011). This may be done through contacting urine with clinoptilolite upon which nutrients are concentrated, leaving a liquid residue which has a high COD content, typically over 4000 mg COD/l, and high salinity over 30 mS/cm. This residual liquid phase has to be treated before disposal for environmental protection and COD concentrations are fit for anaerobic processes, which may act not only to treat the organic fraction but also can generate biogas that may possibly be used for recovering energy.

There are very limited studies in the literature where anaerobic processing is employed to process organic matter in human urine. Previous studies used urine only in co-digestion rather than using it by itself as feed (Kpata-Konan et al 2013; Lavagnolo et al, 2017). No publications were encountered in the literature which investigated anaerobic treatment for processing/revaluating urine as its focus. Additionally, several pieces of work in the literature report possible ammonium release during the anaerobic processing.

The purpose of this paper is to present the preliminary results from an Expended Granular Sludge Bed (EGSB) reactor performing anaerobic treatment to produce biogas from this waste stream as it removes organic matter from urine for environmental protection. This work will focus on the adaptation of the anaerobic sludge with a feeding solution of 25% fresh urine, in an attempt to adapt the anaerobic sludge from a confectionary wastewater treatment plant to highly saline urine. Performance of the EGSB reactor will be investigated not only for organic matter removal but also to see if anaerobic processing will have an effect on NH4+.
2. Materials and Methods

Urine was collected from men’s toilet at Istanbul Technical University. An EGSB was used as the anaerobic reactor with 5.5 l/day of 25% fresh urine feed at a HRT of 11 hr and OLR of 0.72 kg COD/m³.d, where 30% of the volume was filled with granular sludge which was provided from the anaerobic unit of a confectionary plant. The reactor was located in a constant temperature room adjusted to 35–40°C. COD and N were monitored continuously.

3. Results

Under experimental conditions employed in this study, the results revealed that with 25% fresh urine, COD removal efficiency fluctuated in the first month of operation in the startup period, but stabilized thereafter and reached 75% removal efficiency based on soluble COD as an average, whereas the removal efficiency based on total COD was 60% as shown in Table 1. Ammonium release was observed in the effluent at an average of 6%, which was rather low. The amount of methane produced was calculated based on the COD removed per day to show an average of 1.3 l CH₄/day, corresponding to 0.35 l CH₄/g COD and 0.24 l CH₄/l urine.

Table 1. Summary of major experimental results

<table>
<thead>
<tr>
<th>Parameter</th>
<th>COD</th>
<th>NH₄⁺</th>
<th>TKN</th>
<th>pH</th>
<th>Conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Influent</td>
<td>1200</td>
<td>1100</td>
<td>906</td>
<td>2660</td>
<td>7.5</td>
</tr>
<tr>
<td>Effluent</td>
<td>440</td>
<td>300</td>
<td>930</td>
<td>2690</td>
<td>8.1</td>
</tr>
</tbody>
</table>

All in all, the results have revealed that the system was reasonably successful in terms of reducing COD concentrations from about 1200 (1100) mg/l to 440 (300) mg/l as shown in Figure 1 with a reduction of 60% (75%) and the average amount of ammonium release was 6%. These results are significant for determining the best conditions and configuration(s) for combined sorption and anaerobic processes to lead to a concurrent nutrient recovery accompanied by treatment of residual urine while assessing possible production of biogas.

Figure 1. (a) COD concentration in influent and effluent, (b) % COD removal efficiency based on total and soluble COD.

References

Electrodialysis Membrane Fouling, Scaling and Poisoning a Review and a General Approach

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Keywords: electrodialysis; membrane; fouling; scaling; poisoning; polarization

1. Introduction

The objective of this research work is to present a literature review and a general approach of the electrodialysis membrane fouling (EDMF) phenomenon. The electrodialysis membrane fouling (by humic and fulvic acids in natural waters), poisoning (by Fe+++,...), scaling (by CaCO₃, CaSO₄, hydroxides deposits), constitute serious problems to the progress of the ED process. Practical solutions exist to avoid the membrane fouling: the electrodialysis reversal (EDR), the pretreatment by adsorption, acidification … However, there is not a general theory which anticipates and explains the basic mechanisms of the EDMF. The electrodialysis is very well adapted to brakisch waters which are available in large quantities in the North African area. A better understanding of the fouling phenomena will permit a larger use and development of this technology.

2. Materials and Methods

2.1. The Review: Mechanisms and characteristics of the EDMF

The Definitions:

Definitions and classifications has been already proposed by (G. Jonsson and C.E. Boesen, In "Synthetic Membrane Processes ", Academic Press, (1984), 118-129):

- "Fouling" describes the precipitation of colloids, organics or surfactant micelles on the membrane surface.
- "Scaling" defines few solubles salts deposits: carbonates, metal hydroxides.
- "Poisonning" has been already applied to ion exchange resins and extended to ED. It describes the strong fixation (or "complexation") of multivalents ions or large organic ions to the ion exchange fixed sites (SO₃⁻ or NR4+)

The Influence of the Solution Nature:

Influence of organic cations: These studies confirm clearly that poisoning and fouling are not related only to NOM, but to large organic ions, cationic or anionic. From 1971 to 1979, in many papers, T. SATA studied the influence of dodecyl, hexadecyl pyridinium, and polyethylene imine to modify cation exchange membranes surfaces and separate Ca" from Na". Dramatic resistances have been obtained. They increase with the alkyl chain length.

Influence of inorganic ions: The affinity between multivalent ions (Al"", Fe"", Th"""").and ion exchangers is well known. The membrane poisoning is the direct consequence (Urano, T. Ase and Y. Naito, Desalination 51 (1984) 213-226.). ODA YAWATAYA studied the size effect of quaternary ammonium cations, with interesting results.

The Influence of the Current Nature:

Influence of the current reversal(EDR): The anti fouling effects of current reversal are well established and currently applied at industrial scale (W.E. Katz, Desalination 28 (1979) 31-40 .and W.E. Katz, Desalination 42 (1982) 129-139. The main research on mechanisms are from T. SATA, E.J. KOBUS AND P.M. HEERTJES.

Influence of the current pulsations and frequencies (Moon & Al.)


The influence of the salt nature: Urano and Al. have found a very interesting result: NaCl and Na2SO4 solutions have opposite behaviors with the same fouling agent, the Naphtalene monosulfonat NMS"; Then, the composition of the solution (natural waters ...) may influence the severity of fouling. These authors propose an equation to calculate the electric resistance of the membrane and explain the difference between NaCl and Na2SO4 by: " … SO4 was disturbed by NMS much more than Cl because the SO4 is large and combines strongly … ". Unfortunately, this does not explain the basic mechanisms of this difference. We have proposed a mechanism to explain these differences K-E. Bouhidel and M. Rumeau. Desalination (Aug. 2004).

Influence of the industrial waste waters:
With the industrial waste waters where the solution chemistry is many more diversified and complicated than the classical brackish waters (drinking water production). Specific studies on fouling solutes are then necessary. It is illustrated by these recent investigations:


3. Results
This literature review shows that there are not theories which explain the mechanisms of the EDMF. We propose this explanation: the difference of counter ions mobility in their respective membranes promote the weak organic acids (humic and fulvic acids in natural waters) dissociation and influence the ionic migration direction which give a more or less important fouling.
Boron Removal From Industrial Wastewaters by Means of Optimized Sequential Chemical Precipitation and Coagulation Processes

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Keywords: Wastewater treatment, boron removal, precipitation, coagulation, optimization

Abstract

In this work, the removal results of the application of sequential chemical precipitation (CP) and coagulation (CC) over boron containing industrial wastewater were presented. Effect of amount of Ca(OH)₂/B₂O₃ concentration ratio, initial pH and Al₂(SO₄)₃.18H₂O concentration on B₂O₃ removal were investigated using Box-Behnken experimental design. Results show that water has been obtained in a dischargeable quality according to Water Pollution Control Regulation of Turkish Authorities with 95% B₂O₃ removal under optimum operating conditions of 2.12 g Ca(OH)₂/1 g/L B₂O₃ ratio, pH 8 and 18.64 g Al₂(SO₄)₃.18H₂O / L.

1. Introduction

Boron and its compounds are widely used in various manufacturing industries such as additives for borosilicate glass, enamels, cosmetics, leather, textile, paint, wood-processing, detergents, and insecticides, and in the preparation of disinfectants and drugs. Although boron is an essential element for plant growth and is applied directly to the soil for a plant fertilizer, the boron contamination from anthropogenic sources in the environment is becoming a serious problem [1]. According to Water Pollution Control Regulation of Turkish Authorities, the amount of boron in the water to be discharged to the sea should not exceed 500 ppm [2]. Various treatment processes have been developed for boron removal from water, including adsorption, ion exchange, reverse osmosis, electrocoagulation, membrane filtration and precipitation [3]. In the literature, successful results have been achieved with the use of synthetic low amount of boron containing solutions. Since the amount of boron in the wastewater generated by boron industry is very high, these treatment methods do not find a wide use area for themselves. In this work, the results of the application of sequential CP and CC over boron containing industrial wastewater were presented.

2. Materials and Methods

Boron containing industrial wastewater was obtained from a boric acid production plant located in Bandırma/Turkey. Experiments were carried out using original wastewater characteristics at room temperature. Characteristics of the wastewater are given in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>pH</th>
<th>Conductivity (mS/cm)</th>
<th>B₂O₃ (g/L)</th>
<th>SO₄²⁻ (ppm)</th>
<th>Na⁺ (ppm)</th>
<th>Mg²⁺ (ppm)</th>
<th>Al³⁺ (ppm)</th>
<th>Ca²⁺ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>9.46</td>
<td>12.55</td>
<td>11.02</td>
<td>48396.18</td>
<td>4737.33</td>
<td>28.50</td>
<td>1.18</td>
<td>4.75</td>
</tr>
</tbody>
</table>
Experimental procedure of sequential CP and CC are shown in Figure 1.

![Figure 1. Experimental procedure of sequential CP and CC](image)

Box-Behnken experimental design matrix is given below in Table 2.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Ca(OH)$_2$/B$_2$O$_3$ (g/g/L)</th>
<th>pH</th>
<th>Al$_2$(SO$_4$)$_3$.18H$_2$O concentration (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>7</td>
<td>4.14</td>
</tr>
<tr>
<td>2</td>
<td>2.5</td>
<td>9</td>
<td>7.25</td>
</tr>
<tr>
<td>3</td>
<td>2.5</td>
<td>5</td>
<td>7.25</td>
</tr>
<tr>
<td>4</td>
<td>1.75</td>
<td>5</td>
<td>4.14</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>5</td>
<td>7.25</td>
</tr>
<tr>
<td>6</td>
<td>1.75</td>
<td>7</td>
<td>7.25</td>
</tr>
<tr>
<td>7</td>
<td>1.75</td>
<td>5</td>
<td>10.36</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>9</td>
<td>7.25</td>
</tr>
<tr>
<td>9</td>
<td>1.75</td>
<td>7</td>
<td>7.25</td>
</tr>
<tr>
<td>10</td>
<td>1.75</td>
<td>9</td>
<td>10.36</td>
</tr>
<tr>
<td>11</td>
<td>1.75</td>
<td>9</td>
<td>4.14</td>
</tr>
<tr>
<td>12</td>
<td>2.5</td>
<td>7</td>
<td>10.36</td>
</tr>
<tr>
<td>13</td>
<td>1.75</td>
<td>7</td>
<td>7.25</td>
</tr>
<tr>
<td>14</td>
<td>2.5</td>
<td>7</td>
<td>4.14</td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>7</td>
<td>10.36</td>
</tr>
<tr>
<td>16</td>
<td>1.75</td>
<td>7</td>
<td>18.64</td>
</tr>
</tbody>
</table>

3. Results

A regression model was fitted to the experimental data as shown in equation 1.

$$B_2O_{\text{removed}}(\%) = 11.8 + 56.66x_1 + 8.34x_2 - 4.79x_3 - 9.69x_1^2 - 0.563x_2^2 - 2.067x_1x_2 + 0.783x_2x_3$$

(1)

Optimum operating conditions for maximum B$_2$O$_3$ removal were determined according to the fitted model as, 2.12 g Ca(OH)$_2$/1 g/L B$_2$O$_3$ ratio, pH 8 and 18.64 g/L Al$_2$(SO$_4$)$_3$.18H$_2$O and 95% B$_2$O$_3$ removal was achieved.

References

Evaluation of Electro-Fenton Method on Cheese Whey Treatment: Optimization Through Resonse Surface Methodology

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Keywords: Cheese whey, dairy effluent, electro-Fenton, response surface methodology, central composite design

Abstract

In this study, the efficiency of real cheese whey treatment using Electro-Fenton (EF) method and effects of operating parameters on the process were investigated. Central composite experimental design was employed for the optimization of the process and optimum values were obtained as 0.0625 moles Fe⁺², H₂O₂/Fe⁺² molar ratio of 14.48 and 1.41 A current intensity. EF treatment study under optimal conditions yielded 86.75 % COD removal and 6.3 kWh/m³ energy consumption.

1. Introduction

Cheese whey is a by-product of the dairy industry, whose major components are lactose (4.5-5 % w/v), soluble proteins (0.6-0.8 % w/v), lipids (0.4-0.5 % w/v) and mineral salts (8-10 % of dried extract) which result in a heavy organic pollutant load with high chemical and biochemical oxygen values (COD and BOD) of 60-80 g/L and 30-50 g/L, respectively [1-3]. Additionally, high concentrations of suspended solid (SS), chloride and sodium detected in the cheese whey (CW) composition constitutes a potential environmental risk [4]. It is obvious that CW cannot be directly discharged to the environment without any adequate treatment [5]. Raw CW has been treated by means of anaerobic digestion, aerobic digestion, coagulation-flocculation and basic precipitation [4]. Biological processes are very effective in the organic removal despite the difficulty of maintaining stabilized operational conditions and long hydraulic retention times [4,6]. Furthermore, anaerobic operational conditions exhibit the problem of sludge floatation because of the presence of fat. Moreover, caseine necessitates specific microorganisms for its degradation [6]. Chemical processes applied to CW produce clarified effluents with low concentrations of SS, turbidity and nutrients. However chemical processes can reduce the organic matter to approximately half of the initial content, which is higher than direct discharge limit determined by strict legal requirements [4]. Electrochemical treatment may be considered as an alternative process under the conditions when conventional treatment methods fail to reduce pollution [2]. In EF process, in situ production of hydroxyl radical enables high reactivity and powerful non-selective oxidation. A well designed EF process can achieve multiple functions such as electrochemical oxidation, electrocoagulation, electroflootation and/or electoreduction. These processes act synergistically on removing a wide range of complex contaminants [7].

This work is focused on examining the efficiency of real CW treatment using EF method and effects of operating parameters on the process. Statistical models were developed between the amount of Fe⁺² added, H₂O₂/Fe⁺² molar ratio and current intensity as factors and COD removal and energy consumption as responses through Response Surface Methodology and optimization of operational parameters were performed.
2. Materials and Methods

Central composite design was applied to investigate the main variables affecting EF treatment, as well as their interactions. A total of 20 experiments with 8 factorial, 6 axial and 6 central points were performed. Treatment studies were carried out by using 6 graphite electrodes in monopolar parallel arrangement. Each of the factors was coded at five levels \((-\alpha, -1, 0, +1, +\alpha)\) and these levels are given in Table 1 where the maximum and minimum values of parameters were chosen by considering the raw CW characteristics.

Table 1. Levels of independent variables

<table>
<thead>
<tr>
<th>Factor</th>
<th>Level</th>
<th>Level</th>
<th>Level</th>
<th>Level</th>
<th>Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(^{2+}) (moles)</td>
<td>0.0066</td>
<td>0.0180</td>
<td>0.0360</td>
<td>0.0540</td>
<td>0.0654</td>
</tr>
<tr>
<td>H(_2)O(_2)/Fe(^{2+})</td>
<td>3.2845</td>
<td>5.5</td>
<td>9.0</td>
<td>12.5</td>
<td>14.7155</td>
</tr>
<tr>
<td>Current intensity (A)</td>
<td>0.45875</td>
<td>1.25</td>
<td>2.5</td>
<td>3.75</td>
<td>4.54125</td>
</tr>
</tbody>
</table>

3. Results

Experimental results were fitted to statistically significant second order multi-variable polynomial models to point out the main and interaction effects of the factors on responses. Three dimensional (3D) and contour (2D) plots for the predicted responses were formed based on the model function to gain insight about the effect of each variable. The predicted contour plot with the 3D representation is given in Figure 1 for COD removal as an example.

![Figure 1](image-url). Effect of Fe\(^{2+}\) and H\(_2\)O\(_2\)/Fe\(^{2+}\) ratio on COD removal

To achieve the highest treatment performance, the desired goal is maximization of COD removal with minimization of energy consumption. According to multi-objective optimization through overall multi-desirability function, optimum values were obtained as 0.0625 moles Fe\(^{2+}\), H\(_2\)O\(_2\)/Fe\(^{2+}\) molar ratio of 14.48 and 1.41 A current intensity. EF treatment study under optimal conditions yielded % 86.75 COD removal and 6.3 kWh/m\(^3\) energy consumption.

References

Optimization of Combined Electrocoagulation/Electro-oxidation Process for Treatment of Sunflower Oil Industry Wastewater

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Keywords: Hybrid wastewater treatment, electrocoagulation, electro-oxidation, vegetable oil wastewater, response surface methodology

Abstract

Treatment of real sunflower oil industry wastewater using combined electrocoagulation/electro-oxidation (EC/EOx) method was studied and operational conditions were optimized using Box-Behnken experimental design. Optimum values were obtained as 4.02 pH, 2.18 A current intensity, 3 g/L NaCl concentration and 60 min treatment time. EC/EOx treatment study under optimal conditions reduced the COD value to 190.075 mg/L, turbidity to 1.97 NTU with an energy consumption of 5.52 kWh/kg CODr.

1. Introduction

Many technological processes, mainly including pretreatment of oil seeds, manufacturing, refining and modification of oils, are carried out in order to obtain refined vegetable oils from seeds. The operating conditions and processes carried out influence the amount and characteristics of the by-products and wastes formed [1]. When discharged to the environment, oily wastewater affects surface and groundwater resources, endangering aquatic system and human health. The biodegradability of oil in natural ecosystem is low which could cause destruction of useful micro-organisms useful for biodegradation [2,3]. Therefore, it is essential to remove organic pollutants from wastewater before discharge [3]. EC/EOx can be applied to vegetable oil wastewater as a new approach to overcome the drawbacks (low efficiency, long processing time, secondary pollution and high costs) of applied physical, chemical and biological methods including coagulation, flocculation, air floatation, adsorption, reverse osmosis, ultrafiltration, aerobic and anaerobic digestion [3-5]. Electrocoagulation (EC) is a fast and efficient method for wastewaters containing suspended solids, but also an inefficient method for the removal of persistent dissolved organic pollutants [6]. Electro-oxidation (EOx) is able to mineralize persistent organic pollutants completely but also a slow and energy consuming method for the removal of suspended solids [6]. Thus combining the two processes offers a practical hybrid by taking advantage of the synergistic effects [6].

In this study, batch treatment of real sunflower oil refinery wastewater was performed by means of EC/EOx. Box-Behnken experimental design was used to develop mathematical models between independent variables and responses and to optimize the operating parameters to obtain minimum chemical oxygen demand (COD), turbidity and energy consumption.
2. Materials and Methods

Box-Behnken experimental design was applied to form a design matrix using pH, current intensity, NaCl concentration and treatment time as factors whereas final COD, final turbidity and energy consumption were calculated for each run as response. EC/E0x treatment studies were carried out by using 3 aluminum electrodes in bipolar parallel arrangement and 4 graphite electrodes in monopolar parallel arrangement. Levels of independent variables are given in Table 1, where the maximum and minimum values of parameters were chosen by considering the raw wastewater characteristics and past knowledge.

Table 1. Levels of independent variables

<table>
<thead>
<tr>
<th>Factor</th>
<th>Minimum</th>
<th>Centre</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.5</td>
<td>6</td>
<td>8.5</td>
</tr>
<tr>
<td>Current intensity (A)</td>
<td>0.5</td>
<td>1.5</td>
<td>2.5</td>
</tr>
<tr>
<td>NaCl concentration (mg/L)</td>
<td>0</td>
<td>1.5</td>
<td>3</td>
</tr>
<tr>
<td>Treatment time (min)</td>
<td>20</td>
<td>40</td>
<td>60</td>
</tr>
</tbody>
</table>

3. Results

A total number of 27 experiments were performed and experimental results were fitted to statistically significant quadratic models to describe the effects of independent variables on responses. Interacting effect of variables on responses are illustrated by response surface and contour plots. The effects of pH and current intensity on final COD is given in Figure 1 as an example.

![Figure 1. Effect of pH and current intensity on final COD](image)

Multi-objective optimization was achieved successfully through overall multi-desirability function which minimizes the final COD, turbidity and energy consumption simultaneously. Optimum values of the process variables were determined as 4.02, 2.18 A, 3 g/L, 60 min for pH, current intensity, NaCl concentration and treatment time, respectively. EC/E0x treatment study under optimal conditions showed a COD value of 190.075 mg/L, turbidity of 1.97 NTU and energy consumption of 5.52 kWh/kg COD.

References


Innovative MEA Fabrication for Proton Exchange Membrane Water Electrolysis.

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**Keywords**: PEM Water electrolysis, Hydrogen generator, Ozone, PbO2, Electrochemical impedance spectroscopy.

**Abstract**

PEM water electrolysis plays a suitable role in associating renewable energy. The MEA which is used to produce ozone/Hydrogen in PEM water electrolysis gives priority to a coating method. The traditional method wasn't efficient, which is known as ML. This paper will present a different preparation method, known as FL, and compare it with ML. The FL can significantly reduce time and labor and effectively improve production.

1. **Introduction**

This century greenhouse effect has still been increasing, hence to reduce carbon emission through various methods is the global consensus. Developing the clean and renewable energy was the main target by now. However, the major problem of these techniques is that they are affected by the environment and result in that power outputs unstably. Previously, MEA of Ozone/Hydrogen production has been used Decal method for preparing MEA (ML). Nevertheless ML is a time-consuming and labor-intensive method; so the study is to change the anode catalyst ink form and catalyst layer preparation method and proposed (FL), which can not only significantly reduce the workload but also effectively enhance MEA production.

2. **Materials and Methods**

In this study, electrolyte, cathode and electrolyzer were from the commercial resource, exclude anode. Anode preparation.

2.1. Anode preparation

ML coats the catalyst ink layer by layer, and stack with the electrolyte and cathode to constitute MEA. FL is filled catalyst ink in the electrolyzer anode to combine with the electrolyte and cathode.

![Figure 1. Structural simulation of anode after heating (Left) for ML and (Right) for FL](image-url)
2.2. Electrolysis test and analysis

The electrochemical test includes electrolysis, impedance. Through those test methods the different performance between of ML and FL are observed.

3. Results

MEA applies 4.5 V to the assembled electrolyzer and maintains the ambient temperature at 20°C for electrolysis experiments. The activation area of ML and FL both exhibit a stable state, then FL indicates feasibility on performance. After interruption and restoration, ML and FL currents are finally declined by 30.5% and 22.4%, respectively. Obviously, the behaviour will affect ML solid structure, but FL is the free structure, hence the damage is less. In impedance analysis FL in the high frequency indicates that the resistance is nearly ML, however, we can observe the catalytic reaction rate is lower than ML in low frequency. In addition, if concern the labor and time of the process, the FL is potential to replace ML, because ML takes about 30 min to prepare an MEA, while FL only requires about 5 min to finish. Therefore, FL is superior in terms of speed.

References

A Numerical Comparison of Hydrogen Absorption/Desorption Behaviors of Uranium Based Metal Hydride Vessels (MHVs)

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Keywords: Hydrogen storage, Metal hydride, Uranium, Copper-fins, Copper-foams

Abstract

We have applied a three-dimensional transient hydrogen absorption/desorption model developed in our previous works to two different experimental metal hydride vessels (MHVs): one with copper fins and the other with copper foams. The simulation results were corresponded with the experimental data measured from copper-fin-based and copper-foam-based uranium hydride vessels in terms of the vessel temperature evolution and hydrogen absorption/desorption time. Moreover, detailed comparisons of the two types of hydrogen storage vessels were conducted on various MHVs with copper fins or copper foams that were designed to contain the same amount of uranium powder. The detailed analysis of the simulation results clearly showed the characteristics of the hydrogen absorption/desorption and vessel temperature evolution.

1. Introduction

The internal heat transfer capability is one of the key factors for optimizing the design of a MHVs to achieve fast hydrogen charging and discharging performance. Recently, various heat-transfer-enhanced vessel designs have been proposed and subsequently built and tested to improve hydrogen charging and discharging performance [1-2]. In the meantime, a parallel efforts to improve performance by applying heat-transfer-enhancements to MHVs has been made by several MHV modeling groups to simulate hydrogen absorption/desorption processes [3-5].

In this study, the 3-D transient MHV model developed in a previous study [6] was applied to two different experimental copper-foam- and copper-fin-based MHVs. Subsequently, numerical simulations were performed during the hydrogen absorption/desorption process, and the thermal behavior of several MHVs designs was precisely examined at various stages of the hydrogen absorption/desorption process.

2. Materials and Methods

Numerical model

Mass conservation:

\[
\frac{\partial \rho \varrho}{\partial t} + \nabla \cdot (\rho \varrho \dot{u}) = -S_m
\]  

(1)
Metal hydride:

\[
(1 - \varepsilon) \frac{\partial \rho^s}{\partial t} = S_m \tag{2}
\]

In eq. (1), the gas density, \(\rho^g\), can be described by the ideal gas law and \(\varepsilon\) denotes the porosity of the metal hydride vessel. In addition, \(S_m\) is the local hydrogen absorption/desorption rate per unit volume.

Momentum conservation:

\[
\frac{1}{\varepsilon} \left( \frac{\partial \rho^s u}{\partial t} + \frac{1}{\varepsilon} \nabla \cdot (\rho^g u u) \right) = -\nabla P + \nabla \cdot \tau + \rho^g \ddot{g} + S_u \tag{3}
\]

Energy conservation:

\[
\frac{\partial \rho C_p T}{\partial t} + \nabla \cdot (\rho^g C^p_T u T) = \nabla \cdot (k^{eff} \nabla T) + S_T \tag{4}
\]

In this study, a uranium metal hydride vessel was adopted to numerically study the hydrogen absorption/desorption process.

\[
U + \frac{3}{2}H_2 \xrightarrow{\text{absorption}} UH_3 \xrightarrow{\text{desorption}} \tag{UH3}
\]

3. Results

![Figure 1. Three-dimensional contours of (a) uranium hydride temperature and (b) H/M ratio during hydrogen absorption](image)

References


Platinum Nanoparticles Recycling from Fuel Cells With Ionic Liquids

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Keywords: ionic liquids, recycling, nanoparticles, fuel cells.

Abstract

1. Introduction

The cost of a Polymer Electrolyte Membrane Fuel Cell (PEMFC) comes mainly from the platinum nanoparticles which are used as catalyst, it represents 40\% of the stack price for a large-scale production\textsuperscript{1}. It is crucial to reduce their cost to be able to produce cheap cells which could compete with fossil energy.

To reach this goal, one way is the recycling of platinum. For now, platinum is mainly recycled by the use of calcination steps followed by its dissolution in a mixture of strong acids (aqua regia)\textsuperscript{2}. In the case of PEMFC, the burning of the proton-conducting membranes emits hydrofluoric acid (HF), which makes the waste management complicated.

Most of the study makes incremental changes by using less harmful acids, lowering the temperatures or avoiding the HF production but this is not sufficient. The purpose of this study is to propose a breakthrough approach by avoiding the step of the dissolution of platinum by the extraction and stabilization of platinum nanoparticles by ionic liquids\textsuperscript{3}. These solvents, which are salts in a liquid state under 100\(^{\circ}\)C, can stabilize nanoparticles\textsuperscript{4}, have a very low vapor pressure and are stable in a wide range of temperature. Moreover ionic liquids are smart solvents: they can be designed for a wide range of applications. These properties make them recyclable and adapted for the recovery of nanoparticles.

2. Materials and Methods

The work was focused on the choice of the ionic liquid able to penetrate inside the catalyst layer, extract the platinum nanoparticles and stabilize them. The electrode were immersed in the ionic liquids for a specific time and temperature (Figure 1.A). The influence of these parameters were firstly investigated. Twelve ionic liquids and an organic solvent as model (the dimethylsulfoxide) were then compared in the same experimental conditions. These ionic liquids were chosen based on their H-bondings ability, viscosity and molar volume. From these results it was possible to give insights in the type of cations and anions required for the extraction of platinum. MEB characterizations gave indications on the delamination and possible expansion of the catalyst layer of the electrodes; EDX and ICP-OES analyses could give quantitatively and qualitatively the efficiency of the platinum extraction. Finally, from TEM analysis we were able to obtain some characteristics of platinum nanoparticles dispersed in the liquids. To complete this study and to better understand the mechanisms of
the impregnation of ionic liquids inside the ionomer contained in the catalyst layer, Small-
Angle X-ray Scattering (SAXS) studies were performed.

3. Results

The immersion of the fuel cell electrodes in mild conditions in ionic liquids can extract the
platinum from the catalyst layer (EDX/ICP-OES results). Some ionic liquids could indeed
interact with the ionomer and then be able to swell the ionic domains and plasticize the
polymeric aggregates. SAXS results (Figure 1.A) show indeed no difference between
Nafion membrane immersed in ionic liquid (2) and a dry Nafion membrane: the ionic liquid
is not retained inside the ionomer. For ionic liquid (1) a shift of the ionomer peak to the
smaller angles means that the ionic liquid swells the active sites of the ionomer and allows
the platinum extraction. After this step, platinum nanoparticles were found stable in the
selected ionic liquids and detached from their carbon support (Figure 1.B).

Figure 1. A. Protocol for the immersion of electrodes in ionic liquids; B. SAXS profile for a. dry Nafion, a. Nafion membrane immersed in ionic liquid (1), b. Nafion membrane immersed in ionic liquid (2) and c. Dry Nafion; C. TEM picture of platinum nanoparticles stabilized in an ionic liquid after treatment of the catalyst layer.

Mechanisms of the interaction of the ionic liquids and the nanoparticles will be further
discuss and the chemical nature of the ionic liquids able to interact with the nanoparticles
in the context of the recovery of platinum will be presented.

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4 Dupont, J., Scholten, J. D., 2010. On the structural and surface properties of transition-metal nanoparticles in ionic
Optimization of Hardness Removal With Response Surface Methodology from Boron Containing Wastewater Using Bigadic Clinoptilolite

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Keywords: Hardness, Boron, Clinoptilolite, Response Surface Methodology (RSM)

Abstract

In the Bigadiç Etimaden Boron Enterprises, the wastewaters originating from the boron mineral mine base water and the washing of the boron minerals are collected in the wastewater dam, and contain boron and hardness in high concentrations. The raw clinoptilolite obtained from Bigadiç Etimaden Enterprises and modified (HCl and NaOH) clinoptilolite were used for the removal of hardness from this wastewater. Response Surface Methodology (RSM) was used to determine the optimum conditions for the total hardness and calcium hardness removal from the wastewater. Clinoptilolite dosage, contact time, temperature and dilution ratio were selected as independent variables. Using the model, the equations giving the total hardness and calcium hardness which are dependent variables for each of the three adsorbents used are obtained, and the interaction of the independent variables with each other is illustrated by contour graphs. The $R^2$ values were above 0.90. The highest removal efficiency and adsorbent capacity were obtained with clinoptilolite modified by NaOH.

1. Introduction

The boron element has many uses and is a critical parameter in terms of environment. It has a toxic effect on plants, animals and humans when it is above the limit value in the waters, and must be treated [Wang et al, 2014; Yilmaz et al, 2005; Köse and Oksüz, 2009; Tu et al, 2010; Kavak, 2009].

When membrane processes are selected as a treatment technique, the high hardness besides the boron element contained in the waters causes stratification and clogging on the membrane surface. Therefore, the pre-treatment should be done to remove the hardness. The conventional pre-treatment methods increase the cost of boron removal by Reverse Osmosis (RO) method [Duman and Ozmetin, 2014].

Zeolites are aluminosilicate minerals that contain interchangeable alkali and alkaline earth metal cations (normally $\text{Na}^+$, $\text{K}^+$, $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$) in addition to the water in the structural frameworks. In many regions of the World, one of the most amount of natural zeolite types which is clinoptilolite consists both large mineraloid sedimentary deposits and high purity. Clinoptilolite is one of the most abundant natural zeolite species found in relatively large pelitic sedimentary deposits of sufficiently high purity in many parts of the world. [Gunay, 2007]. One of the natural zeolite is clinoptilolite which is used to remove cations[Demir et al., 2002]. The hardness is due to the polyvalent metal cations in the water [Sawyer, 2013].
In this study, it was aimed to determine optimum conditions by using raw and modified forms of Bigadiç clinoptilolite which is a cheap and abundant adsorbent for the removal of hardness from boron containing wastewaters.

2. Materials and Methods

The wastewater used in the study was taken from Bigadiç Etimaden Bor Enterprises wastewater dam. Characterization of wastewater is given in Table 1. In order to eliminate the total hardness and calcium hardness, Bigadic clinoptilolite which is abundant and cheap material is used. In the study, the raw and modified Bigadiç clinoptilolite in HCl and NaOH solution were used. The experiments were carried out under conditions determined by RSM. The clinoptilolite dose, contact time, temperature and dilution ratio were chosen as independent variables, total and calcium hardness removal efficiency and clinoptilolite adsorption capacity were chosen as dependent variables.

Table 1. Characterization of wastewater

<table>
<thead>
<tr>
<th>pH</th>
<th>Conductivity (µS/cm)</th>
<th>Total Hardness (mg CaCO₃/L)</th>
<th>Calcium Hardness (mg CaCO₃/L)</th>
<th>Boron (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.66</td>
<td>2137</td>
<td>658,784</td>
<td>211,68</td>
<td>602,89</td>
</tr>
</tbody>
</table>

3. Results

Using the model, the optimum conditions for removal of the total hardness and calcium hardness from the wastewater and the effective parameters of the removal were determined. The equations giving the remediation and adsorption capacity were obtained. In the optimum conditions obtained by RSM, validation experiments were carried out and results consistent with the model were obtained.

References

The Pyrolysis Bioproduct Characterization and Thermogravimetric Analysis of Waste Corn

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Keywords: Bio-products, pyrolysis, waste corn.

Abstract

In this study, the pyrolysis characteristics of corn waste were investigated by thermogravimetric analysis (TGA) and the kinetic parameters were calculated by Ozawa-Flynn-Wall and the Kissinger-Akahira-Sunose methods. However, corn wastes were pyrolysed in laboratory scale pyrolysis system without catalyst. The obtained from pyrolysis bio-char and bio-liquid products were characterized by elementel, BET, calorific value and GC-MS analysis.

1. Introduction

Corn waste whose main chemical components contain abundant cellulose, hemicellulose and lignin is one of the by-products of grain crops (Li et al., 2016). So far the utilization of waste corn is not high, except for a limited comprehensive utilization as feed, fertilizer, industrial raw materials, fuel, and so forth (Xu et al., 2016). The pyrolysis process offers an alternative way to convert to useful products. Pyrolysis is a thermal decomposition of organic substances under oxygen-absence circumstances into various phases: liquid products (condensable vapors at cooling temperature); carbon-rich solid residues (bio-char); gaseous products (syngas which were not condensable gases) (Bridgwater, 2012; Butler et al., 2011).

2. Materials and Methods

The decomposition behavior of corn waste samples was studied by the thermogravimetric simultaneous thermal analyzer. Another pyrolysis experiment was carried out in a lab scale fixed bed reactor at heating rates of 3°C/min and 5°C/min. The collected bio-char and bio-liquid products were analysed. The specific surface area of bio-chars were determined using an Micromeritics TriStar II PLUS BET (Brunauer-Emmett-Teller) analyzer. The calorific values of bio-char and bio-liquid products were measured by calorimeter bomb. The bio-liquid fraction were analysed by using a gas chromatography-mass spectrometry (GC-MS).

2.3. Kinetic Models

In this work, the Ozawa-Flynn-Wall (OFW) method and the Kissinger-Akahira-Sunose (KAS) method were used to calculate the apparent activation energy with three different heating rates, as expressed in following Eqs. (1) and (2) (Fang et al., 2018), respectively:

\[
\log(\beta) = \log \left[ \frac{AE}{RG(\alpha)} \right] - 2.315 - 0.457 \frac{E}{RT} \tag{1}
\]

\[
\ln(\frac{\beta}{R^2T^2}) = \ln \left[ \frac{AE}{RG(\alpha)} \right] - \frac{E}{RT} \tag{2}
\]

where \(\alpha\) is the conversion degree, \(T\) is the reaction temperature, \(E\) is the activation energy, \(A\) is the pre-exponential factor, \(R\) is the universal gas constant, \(\beta\) is the heating rate (defined as \(dT/dt\)) and \(G(\alpha)\) is the temperature-independent function of reaction model.
3. Results
3.1. Thermogravimetric analysis of corn wastes
The mass loss (TG) and derivative mass loss (DTG) curves of corn wastes at the heating rate of 20°C/min and 50°C/min under CO₂ atmosphere were shown in Fig. 1. The crossover point between two stages is defined as the midpoint of the line between two tangent lines (Pickard et al., 2013). For 20°C/min and 50°C/min heating rates, the final temperature of pyrolysis is acquired when the biomass loss is 94.8% and 99.6% of the total weight loss, respectively.

![Fig. 1. TG curves at the heating rate of (a)20 °C/min and (b) 50°C/min of corn wastes](image)

3.2. Characterization of pyrolysis products
The biochar characterization parameters were given in Table 1. According to these results, when pyrolysis temperature increased, C and O contents of bio-chars increased due to increasing of decomposition. As carbonic structure developed, higher heating values (HHV) and lower heating values (LHV) increased. BET values of bio-char samples are between the 57-64 m²/g .

<table>
<thead>
<tr>
<th>Properties of bio-char</th>
<th>3 °C/min</th>
<th>5 °C/min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300</td>
<td>500</td>
</tr>
<tr>
<td>C (wt.%)</td>
<td>91.21</td>
<td>94.42</td>
</tr>
<tr>
<td>H (wt.%)</td>
<td>1.14</td>
<td>0.92</td>
</tr>
<tr>
<td>N (wt.%)</td>
<td>0.44</td>
<td>0.51</td>
</tr>
<tr>
<td>O (wt.%)</td>
<td>3.41</td>
<td>3.27</td>
</tr>
<tr>
<td>HHV (MJ/kg)</td>
<td>49.41</td>
<td>49.85</td>
</tr>
<tr>
<td>LHV (MJ/kg)</td>
<td>48.95</td>
<td>49.45</td>
</tr>
<tr>
<td>BET (m²/g)</td>
<td>57.85</td>
<td>61.22</td>
</tr>
<tr>
<td>V_pore (cm³/g)</td>
<td>0.0521</td>
<td>0.0678</td>
</tr>
</tbody>
</table>
References
Abstract

Treatment of heavy metals is required to protect the nature. Adsorption, is an alternative method, has been still under investigation giving chance to regain of discharged heavy metals. In this study, alginates (A), natural biopolymers from brown algae, are applied together with clinoptilolite (C) in bead forms for heavy metal removal from a synthetic wastewater. Results showed that A-C beads were efficient for the treatment of mixed metal solution. Adsorption of Pb$^{2+}$ was found better compared to Cu$^{2+}$ and Cd$^{2+}$. Also, evaluation of equilibrium kinetics was compatible with pseudo second order model.

1. Introduction

The uncontrolled increase in human population and industrialization resulted environmental pollution. Heavy metals widely used in different industries are hazardous substances. When they are discharged without proper treatment, heavy metals can be toxic to the environment, accumulate in food chain. Therefore, they are serious pollutants required to be removed.

Although there are lots of methods used for heavy metal removal from water, adsorption can be a good alternative if the adsorbent is natural, easy to find and economic. Recently, studies focused on natural adsorbents. Thus, alginates are getting attention, which can capture metals particularly by carboxyl groups in their structure. On the other hand, since alginate like cheap adsorbents’ treatment capacities are not enough to use them in real applications, researches are continued to seek more efficient adsorbents. In this study, in order to increase adsorption capacity of alginate, clinoptilolite, which is a zeolite having abundant source in Turkey, was selected. In this context, it was aimed to remove Cu$^{2+}$, Cd$^{2+}$, Pb$^{2+}$ heavy metals from a synthetic wastewater by using alginate-clinoptilolite (A-C) beads in batch reactors.

2. Materials and Methods

Effects of clinoptilolite size, A/C ratio, pH, heavy metal concentrations and adsorption kinetics were investigated in the study. Only the results obtained from the evaluation of adsorption kinetics are presented here. For this purpose, alginate (2%) was combined with clinoptilolite, from Manisa-Gördes, to form A-C beads by dropping into CaCl$_2$ solution. Adsorption kinetics were determined using 100 mg A-C beads subjected to a mixture of Cu$^{2+}$, Cd$^{2+}$, Pb$^{2+}$ as 100 mg/L solution for each at pH 4 and 150 rpm by time dependent sampling during 48 hours. All were acidified and cooled until analysis. The data were evaluated by using common methods such as pseudo first and second order models.
3. Results

Adsorption of heavy metals are observed to be faster during early times of the experiments (Figure 1). Equilibrium times for Cu\(^{2+}\) and Cd\(^{2+}\) were found 24 hours while it was 8 hours for Pb\(^{2+}\). Similar results were obtained by Türe et al (2017). It seems the A-C beads prefer to take Pb\(^{2+}\) more efficiently since almost all of the metal can be removed from the solution. This is probably explained by the difference in the affinity of metals towards the composite adsorbent. Furthermore, the maximum removal efficiencies are calculated for Cu\(^{2+}\) and Cd\(^{2+}\) as 82 and 74 %, respectively. Adsorption capacity is also higher in the case of Pb\(^{2+}\) being around 48 mg Pb\(^{2+}\)/g A-C beads. On the other hand, adsorption kinetics are determined to compatible with pseudo-second order model (Figure 2). Adsorption rate constants for the metals are changing in the range of 0.02 – 0.047 mg/g.min. Likewise, Sigdel et al (2017) also showed that adsorption of Cd\(^{2+}\) can be expressed by pseudo second order model.

![Figure 1. Heavy metal removal evaluation by time](image1)

![Figure 2. Pseudo first order (left) and pseudo second order (right) model](image2)

**References**


Abstract

Use of Ecotoxicology Tools Within the Environmental Footprint Evaluation Protocols: The Case of Wastewater Treatment Plants

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Keywords: Bioassays; Daphnia magna; Freshwater; PEF/OEF; Raphidocelis subcapitata; Vibrio fischeri

Abstract

This work focuses on the application of the protocol for the assessment of the environmental footprint of products and organizations, performed accordingly with the prescriptions of the European Commission Recommendation 2013/179/EU. In effect, although scientific and technical literature already reports some example cases carried out in several industrial fields, this methodology has not been run yet for the evaluation of the environmental performances of a wastewater treatment plant. The research has been carried out on a real scale plant, by acquiring, in parallel, operation data, chemical, physical and biological parameters throughout a two weeks-campaign. Effluent toxicity towards the aquatic ecosystem was measured by adopting a multitiered approach, being test organisms crustaceans, bacteria and algae, respectively. The protocol for the evaluation of the environmental footprint was followed by considering as input data either the results of the chemical, physical and biological analyses or those deriving from the bioassays execution. The findings clearly illustrate the unvaluable importance of bioassays in the process of evaluation of the environmental impact of any work, together with the need of combining different tests based on specific endpoints and involving organisms playing different trophic roles.

1. Introduction

Life Cycle Assessment (LCA) is a standardized and sophisticated tool that allows to quantify and compare the potential impacts, associated to the consumption of resources and emissions of pollutants in the environment, occurring along throughout the life cycle of products, services or processes (from the extraction of raw materials to the final disposal). Although the LCA protocol was defined by ISO 1440 and 1444 standards (ISO, 2006a, 2006b), a range of several methodological approaches, such as the Life Cycle Impact Assessment (Lehmann et al., 2015), has been explored yielding quite different conclusions (Corominas et al., 2013a). The Recommendation 2013/179/EU establishes a new protocol for an overall assessment of the environmental footprint of products and organisations, by harmonizing and overcoming the previous conventional tools. Although several PEF/OEF studies focus on products and organizations in different industrial sectors (e.g. Six et al., 2017), there is still lack of knowledge and experience regarding the application to WWTPs.
In life-cycle-based methodologies, the assessment of the effect on the different impact categories is based on mass flows of pollutant discharged in the environment or resources used. The evaluation of the impact of a WWTP effluent cannot be merely based on the quantification of emission loads, calculated by adopting a “compounds-based” methodology. Several studies have suggested that the constrains of chemical “single substances” approach can be overcome by carrying out multi-tiered biological assays, which can measure the impact of a stream (Escher et al., 2014) more accurately. Therefore, bioassays allow to better simulate the actual sceneries, by taking into account possible additive, subtractive and synergistic effects on a living system.

This paper presents the results of a study, still in progress, having its premises on a previous work (Pedrazzani et al., 2018). In particular, the environmental footprint of a real scale WWTP has been evaluated by applying the PEF/OEF protocols. Furthermore, we propose an innovative procedure for the integration of the results of chemical, physical and biological monitoring with the findings of ecotoxicity tests.

2. Materials and Methods

The assessment of the environmental footprint of a real scale WWTP (design size 60,000 p.e.) was performed with the software SimaPro (version 8.2.0) in which the environmental footprint categories and impact assessment models were selected, in order to ensure the compliance with the Recommendation 2013/179/EU. The calculation of the 15 environmental footprint indicators, defined by the PEF/OEF protocols, was based on mass flows of pollutants discharged into the environment. Data were primary (measured directly in the field) and consisted in effluent characteristics (in terms of flowrate, organic and inorganic compounds concentration) and on the amount of chemicals and energy used, as well of waste produced. Likewise, toxicity tests were performed on the same samples. Standard methods were always followed. The results of the assessment of baseline toxicity exhibited by the aquatic organisms were converted into a biological equivalent concentration of reference substances. Thus, the equivalent load of reference substances was used instead of the pollutants loads, derived from the routine monitoring, for the assessment of the impact towards freshwater ecosystem.

References


Environmental Burdens of Cataphoresis Process

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Abstract

The automotive industry has an important role in Turkish manufacturing sector. In 2017, more than 1 million vehicles are produced in Turkey (AMA, 2017). Automotive production processes are basically divided into four: press, welding, paint, assembly. Painting process is among the most important processes in the manufacturing train from both quality requirements and environmental concerns. The aim of this process is to protect the surface by coating it. Diverse kind of coating methods are applied. Spray painting and cataphoresis are generally used in industrial painting operations. Although cataphoresis process is identified as a best available technology, significant environmental impacts are generated from it.

In this context, this study focuses on appraising the environmental burdens of the widely used cataphoresis process in automotive industry. For this purpose an actual plant with an annual production of around 6,100 vehicles composed of trucks and busses is investigated by adopting life cycle assessment (LCA) approach. Data collection is performed on the cataphoresis process of the industry. The inventory data was analyzed by GaBi 7.3 software. Functional unit is 1m² of coated metal surface. System boundaries consist of cataphoresis pretreatment and electrocracking processes. The impacts categories considered are climate change (CC), acidification potential (AP), particulate matter and respiratory inorganics (PM), photochemical ozone formation (POF), ecotoxicity freshwater potential (EP), eutrophication (terrestrial, freshwater and marine), human toxicity potential (HTP), ozone depletion potential (ODP), and resource depletion (water).

The total energy consumption of the investigated cataphoresis process is approximately 12.5 kWh/m². The environmental impacts obtained are in accordance with the literature values. The highest shares to the environmental impacts come from ED coating and UF water rinse tanks. The contribution of transportation to environmental impacts is less than 2%. The results shows that energy consumption effects almost all environmental impact categories. Therefore, four different energy scenarios are applied to show the effect of energy sources: wind, photovoltaic, hard coal and Turkish grid electricity. The results indicates the usage of wind energy lowers all impacts.

References

Olive Pomace Pyrolysis After Chemical Preprocessing

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Keywords: Olive pomace, chemical preprocessing, pyrolysis, calcium hydroxide

Abstract

In this study, Ca(OH)$_2$ preprocessing effect on Olive pomace (OP) pyrolysis product yields and chars’ inorganic amounts was revealed. Chemical preprocessing before pyrolysis led to liquid decrement and char increment. K and Ca amounts in pyrolysis chars showed an opposite trend when Ca(OH)$_2$ dosage was increased in preprocessing.

1. Introduction

Olive pomace (OP) is the solid waste of olive oil generation process and mainly comprises of olive pits, olive skin, water, pulp and oil. OP generally contains polysaccharides, proteins, other pigments, ligno-cellulosic polyalcohols, polyphenols and fatty acids (Gianico et al., 2013). Therefore, waste management of OP should be done effectively due to its contents. Thermochemical conversion processes, especially pyrolysis, have been used widely in OP waste management. There are some pretreatment methods before pyrolysis. Alkaline pretreatment has been used prevalently due to having less severe circumstances and more effective way for solubilization of lignin. It includes bases usage applied to provide enhancement in pyrolysis bio-oil amount and characteristic for lignocellulosic substances pretreatment (Carpenter et al., 2014). However, the effect of alkali pretreatment on OP pyrolysis has not been studied yet. Therefore, in this study, the effects of calcium hydroxide preprocessing on pyrolysis was studied since this is one of the effective method for agglomeration prevention in lignin biomass pyrolysis and it is less expensive than sodium, ammonium, potassium hydroxide (Sánchez et al., 2011). Moreover, effects of calcium hydroxide preprocessing on both pyrolysis product yields and inorganic components of pyrolysis chars were revealed.

2. Materials and Methods

Two-phase wet OP sample was taken from olive mill facility (Mersin) soon after olive picking season. Firstly, 100 grams OP was pyrolyzed at 600°C-1°C/min heating rate with 30 minutes retention and at 600°C-5°C/min heating rate without retention. Secondly, Ca(OH)$_2$ alkali pretreatment was applied to OP before pyrolysis. Ca is one of the inorganics exist in raw OP therefore Ca(OH)$_2$ doses were adjusted in the manner that inherent Ca amount increases by 2 and 3 times. 3.7 and 6.9 grams Ca(OH)$_2$/100 grams OP was added directly to biomass and slurry was mixed with stirrer for 5 minutes to satisfy homogeneous mixture. Then the sample was pyrolyzed at the same pyrolysis conditions. Pyrolysis products were collected separately and product yields were determined as weight. Inorganic components in raw OP and in pyrolysis chars were determined with Thermo Fisher Scientific 6000 series ICP-OES after microwave preprocessing.
3. Results
Mixing OP with Ca(OH)₂ resulted in liquid decrement and char increment at both pyrolysis conditions, however the highest effect of chemical preprocessing on OP pyrolysis was obtained at 5°C/min heating rate without retention pyrolysis condition (Figure 1). While addition of Ca(OH)₂ enhanced gas formation at the shortest pyrolysis duration, its effect on gas product became reversed at the longest pyrolysis duration. All these changes about product yields can be explained by that effects of Ca(OH)₂ on biomass pyrolysis product yields can be variable based on pyrolysis process and pyrolysis duration. In Ca dehydration process water is released (Wang et al., 2010) and this water differently affects pyrolysis product yields as depend on pyrolysis condition. Increment in Ca(OH)₂ dosage mostly did not affect OP pyrolysis product yields too much (Figure 1).

![Figure 1. Effects of calcium hydroxide preprocessing on 100 g OP pyrolysis product yields](image)

Chemical preprocessing also affected inorganic compound distribution in OP pyrolysis. Pyrolysis chars obtained after chemical preprocessing included mainly K and Ca and other major components were found at very low quantities (Figure 2). The first conspicuous point while K in char decreased, Ca increased excessively compared to OP pyrolysis chars. Moreover, increment in Ca(OH)₂ amounts in chemical preprocessing resulted in Ca increment and K decrement in chars at longest and shortest pyrolysis duration. Therefore, it can be inferred that Ca(OH)₂ supports passing of K to pyrolysis liquid. Furthermore, longer pyrolysis duration caused Ca decrement and K increment.

![Figure 2. Chemical preprocessing effect on inorganic quantities of char obtained at 600°C (t: retention time after pyrolysis process)](image)

References

Acknowledgements
This study was financially supported by Selcuk University BAP-18101003.
Utilization of Sulfonated Polystyrene in the Treatment of Waste PS Plastic Washing Wastewater

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Keywords: Coagulation-flocculation, PS, waste PS sulfonation

Abstract

Polystyrene (PS) waste washing wastewater contains high concentrations of, turbidity, Chemical Oxygen Demand (COD), Suspended Solids (SS) and oil-grease that lead to an increase in the pollution load of wastewater treatment plant. In this study, a polymeric material acting as flocculant (FSPS) was synthesized from waste PS by sulfonation and it was used in coagulation-flocculation treatment of PS washing wastewater. Effects of pH were studied at pH 3-13 interval. Alum and FeCl₃ were used as conventional coagulants. The performance of synthesized FSPS was compared with conventional flocculant, polyelectrolyte (PE). The produced FSPS resulted in higher and/or close performances with PE.

1. Introduction

In developed countries, plastic consumption has grown remarkably over the decades (Mudgal et al., 2013). Industry is increasingly moving towards reusing and reprocessing plastics for economic and environmental reasons, with many companies developing technologies and strategies for recycling plastics (Nhamo et al., 2016). The quality of mechanically recycled plastic waste is affected by prewashing of the waste. Therefore, washing effluents are the polluted wastewaters that need to be treated. The coagulation-flocculation is a process commonly used for their treatment. The flocculation performance depend on the choice of flocculant. A number of flocculants are commercially available, but some of them have been received attention for their negative environmental consequences and potential health impacts (Jin et al., 2013) such as their potential contribution to Alzheimer's disease (Divakaran et al., 2001) and large scale sludge production (Renaut et al., 2009). Sulfonation of waste PS had been developed as a PS recycling method and by this method a flocculant can be produced (Vink, 1981; Bekri-Abbes et al, 2007). In this study, sulfonated PS was synthesized from waste PS and its effectiveness in the coagulation-flocculation treatment of waste PS washing wastewater was investigated.

2. Materials and Methods

PS waste was crushed to <8 mm and washed in three steps as in real industrial washing (Santos, 2005). In the first step, PS waste was boiled in 42% of NaOH at 90°C for 10 minutes, in the second and third steps, the rinsed with tap water at 90°C for 10 minutes and then the waste was left to dry. The effluents of the three washing step were collected as wastewater.

Sulphonated PS flocculant was synthesized by the method of Vink (1981). Accordingly crushed waste was dissolved in cyclohexane. P₂O₃ was dissolved in H₂SO₄. The two
solutions were mixed and kept at 40°C for an hour. The sub-phase was separated, distilled water was slowly added to the mixture of supernatant polymer. Powdery FSPS flocculant was obtained by making the mixture dried at 40°C for a day.

In Jar-tests, Alum and FeCl₃ were used as coagulants (at doses of 15-1000 mg/L), and synthesized FSPS and conventional polyelectrolyte (PEL) (at doses of 5-50 mg/L) were used as flocculants. After rapid mixing, slow mixing and then settling for 1 hour, samples were taken from the supernatants and turbidity, COD, SS and Oil-Grease analyses were performed. The two most efficient flocculant doses were selected and effects of pH on treatment performances were studied at pH 3-13 interval.

3. Results

In the preliminary experiments, only coagulant was dosed and final removal efficiencies of the parameters were determined. Accordingly 1000 mg/L Alum and FeCl₃ dosage was selected and fixed at subsequent experiments. In the second stage the flocculent concentrations were changed by keeping other conditions the same. At this stage Alum+20 mg/L and 40 mg/L FSPS, Alum+40 mg/L and 50 mg/L PEL, FeCl₃+5 mg/L, 10 mg/L both FSPS and PEL were determined as the two most efficient flocculant doses. Under these dose conditions, effects of pH on the treatment are indicated on Figure 1 (FeCl₃ data not shown here). At pH 3, Alum+20 mg/L FSPS resulted in 96% turbidity, 75% COD, 95% SS and 65% oil-grease removals, while at the original pH of the wastewater (13±1) FeCl₃+5 mg/L FSPS, these efficiencies were 88%, 71%, 93% and 83%, respectively. At pH 9, Alum+40 mg/L FSPS resulted in 98% turbidity, 77% COD, 97% SS and 67% oil-grease removals, however, at pH 7, FeCl₃+5 mg/L FSPS, they were 82%, 81%, 96% and 52%, respectively.

Figure 1. Change of parameter values with pH for Alum+FSPS in PS washing wastewater

Acknowledgement

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References

Thermoplastic Wastes Pyrolysis Char in the Epoxy Composite as Filler

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Keywords: Mixed thermoplastics, pyrolysis, char, epoxy composite

Abstract

Thermoplastic wastes are generally collected in mixed form and types of plastics can be separated in the transfer stations when needed. In this study, mixed thermoplastics were pyrolysed and pyrolysis char was used as filler in epoxy composite (ER) matrix. Effects of pyrolysis temperature and filler dosage on ER properties were investigated. As a result, neat ER mechanical properties were improved and semi-conductor composite was obtained.

1. Introduction

Pyrolysis degrades the solid waste into gaseous, liquid and solid fractions. Pyrolysis gases and liquids have been commonly used either as fuel or as feedstock. However, use of pyrolysis solid fraction, char, is rather rare. The most common lab-scale trials are on its utilization as adsorbent (Pellera and Gidarakos, 2015). Recently, several studies investigated the utilization of plastics pyrolysis chars as filler (additive) in composites for HDPE, LDPE, PET, PP and PS type thermoplastic waste chars (Sogancioglu et al, 2017 a and b; Sogancioglu et al, 2016; Yel et al, 2017; Yel et al, 2016; Yucel et al, 2015; Ahmetli et al, 2013). In waste management, separation of collected plastic wastes is a cost, time and labor consuming process. In this study, mixed thermoplastic wastes were directly pyrolysed without separation and/or pre-washing and the pyrolysis char was used as filler in epoxy composite (ER). Effect of filler dose and the pyrolysis temperature that it was obtained on the ER properties were investigated.

2. Materials and Methods

Thermoplastic wastes were collected from municipal waste separation center, main impurities (paper, etc) were removed and they were crushed to less than 8 mm. Batch pyrolysis was applied under inert (nitrogen) atmosphere at 5°C/min heating rate. At the end of pyrolysis the solid residue remained in the reactor was collected as char sample. In the composite matrix DGEBA type commercial epoxy resin-NPEL128 (EEW 190 g/eq), Epamine PC17 curing agent (Konuray Chemical Co) and 2,4,6-tris (dimetilaminometil) fenol (Sigma-Aldrich) accelerator were used. ER production method reported by Sogancioglu et al, (2017a) was applied. Pyrolysis chars (particle size<63µm) obtained at different temperatures (300-700°C) were added as filler at 10, 30 and 50% dosages. Electrical conductivities of the composites were measured by four-point probe technique. Shore Durometer TH 210 tester was used for measuring hardness of the composite. The stretch resistance properties were determined by the Stretch and Pressing Equipment TST-Mares/TS-mxe. Thermogravimetric analyses (TGA) were performed using a TGA analyzer, under nitrogen atmosphere at atmospheric pressure.
3. Results

Pyrolysis char filler decreased the % elongation at break as compared to neat ER. 500 and 600°C char filler at 10% resulted in increase in tensile strength of the composites (Table 1). Similarly, elasticity modulus and hardness values of composites were increased by char filler. These indicated that char filler can improve physical properties of ER, char pyrolysis temperature and dosage have influence on the composite quality.

Table 1. Effects of char pyrolysis temperature and char dose on ER properties (IDT: initial decomposition temp, SDT: second decomposition temp)

<table>
<thead>
<tr>
<th>Pyrolysis Temp. (filler, weight%)</th>
<th>Elongation at break %</th>
<th>Tensile strength, MPa</th>
<th>E-modulus GPa</th>
<th>Hardness Shore D</th>
<th>Elec. conductivity S/cm</th>
<th>IDT</th>
<th>SDT</th>
<th>Water absorb rate, mg/g comp/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat ER</td>
<td>0.721</td>
<td>86</td>
<td>6.2</td>
<td>80</td>
<td>10^{14}</td>
<td>125</td>
<td>275</td>
<td></td>
</tr>
<tr>
<td>ER/Mixed Plastic waste composites</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300°C (10%)</td>
<td>0.759</td>
<td>80</td>
<td>8.1</td>
<td>80</td>
<td>1.94 × 10^{5}</td>
<td>195</td>
<td>290</td>
<td>0.0111</td>
</tr>
<tr>
<td>300°C (30%)</td>
<td>0.651</td>
<td>73</td>
<td>7.4</td>
<td>81</td>
<td>1.88 × 10^{5}</td>
<td>235</td>
<td>335</td>
<td>0.0140</td>
</tr>
<tr>
<td>300°C (50%)</td>
<td>0.472</td>
<td>54</td>
<td>5.5</td>
<td>79</td>
<td>2.01 × 10^{5}</td>
<td>285</td>
<td>380</td>
<td>0.0486</td>
</tr>
<tr>
<td>400°C (10%)</td>
<td>0.559</td>
<td>81</td>
<td>9.3</td>
<td>79</td>
<td>2.13 × 10^{5}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400°C (30%)</td>
<td>0.487</td>
<td>78</td>
<td>7.3</td>
<td>80</td>
<td>1.39 × 10^{5}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400°C (50%)</td>
<td>0.445</td>
<td>75</td>
<td>7.7</td>
<td>80</td>
<td>1.56 × 10^{4}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500°C (10%)</td>
<td>0.585</td>
<td>96</td>
<td>10.0</td>
<td>80</td>
<td>1.45 × 10^{5}</td>
<td>195</td>
<td>290</td>
<td>0.0184</td>
</tr>
<tr>
<td>500°C (30%)</td>
<td>0.502</td>
<td>80</td>
<td>9.5</td>
<td>82</td>
<td>2.82 × 10^{5}</td>
<td>235</td>
<td>335</td>
<td>0.0143</td>
</tr>
<tr>
<td>500°C (50%)</td>
<td>0.394</td>
<td>85</td>
<td>8.9</td>
<td>83</td>
<td>1.25 × 10^{4}</td>
<td>285</td>
<td>380</td>
<td>0.0282</td>
</tr>
<tr>
<td>600°C (10%)</td>
<td>0.438</td>
<td>106</td>
<td>7.8</td>
<td>82</td>
<td>1.04 × 10^{5}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600°C (30%)</td>
<td>0.351</td>
<td>88</td>
<td>9.0</td>
<td>82</td>
<td>9.08 × 10^{5}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600°C (50%)</td>
<td>0.307</td>
<td>72</td>
<td>9.1</td>
<td>81</td>
<td>1.79 × 10^{4}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>700°C (10%)</td>
<td>0.474</td>
<td>81.6</td>
<td>9.5</td>
<td>83</td>
<td>2.77 × 10^{5}</td>
<td></td>
<td></td>
<td>0.0177</td>
</tr>
<tr>
<td>700°C (30%)</td>
<td>0.437</td>
<td>77</td>
<td>9.6</td>
<td>84</td>
<td>1.32 × 10^{5}</td>
<td></td>
<td></td>
<td>0.0213</td>
</tr>
<tr>
<td>700°C (50%)</td>
<td>0.346</td>
<td>56</td>
<td>6.4</td>
<td>85</td>
<td>1.67 × 10^{4}</td>
<td></td>
<td></td>
<td>0.0240</td>
</tr>
</tbody>
</table>

Neat ER is an insulating material. However, by the addition of plastics pyrolysis char filler, the material become semi-conductor with increasing conductivities (Table 1). Pyrolysis temperature slightly affect the composite conductivities, however, as filler dosage increased, conductivities increased as well. At pyrolysis temperatures 500°C or higher, aromaticity and carbonized material increase in the char content can be the reason for this. Besides these mechanical and electrical properties, thermogravinery also indicated that by adding char filler, more durable coposites were produced such that as filler dose increased, FDS and SDS temperatures increased as compared to neat ER (Table 1). Composites with filler has very low water absorption rates, although the char filler has 22-35 Å pore size distribution. Increased filler dosage increased water absorption rate. The composites reach water saturation level in around 210-306 hours. The study indicated that, mixed thermoplastics can directly be pyrolysed to use char as ER filler to obtain good quality semi-conductor composites.

Acknowledgement

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Sogancioglu, M., Yel, E., Ahmetli G, 2017(a). Pyrolysis of waste high density polyethylene (HDPE) and low density polyethylene (LDPE) plastics and production of epoxy composites with their pyrolysis chars, Journal of Cleaner Production 165, 369-381.


Evaluation of Nutrient Removal and Recovery by Electrochemical Process from Human Urine

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Keywords: Urine, nutrient recovery, nitrogen, phosphorus, electrochemical processes, Sustainability

Abstract

Human urine is of considerable value or source for two reasons. Firstly, there has been a decrease in nutrients in the world and urine contains a considerable amount of nutrients and secondly, it exists everywhere the person lives.

The most important source of pollution in domestic wastewater is human waste and in other words human urine (yellow water). The separation of human urine at source will reduce the pollution value of wastewater. On the other hand, the recovery of nutrients in yellow water will also provide meaningful benefits for agricultural sustainability. This paper has reviewed the nutrients removal and recovery from human urine by various electrochemical systems.

1. Introduction

Human urine mainly contains sodium chloride (NaCl), urea (CO(NH₂)₂), potassium (K), sulfate (SO₄), calcium (Ca) and phosphate (PO₄). Urine also contains a considerable amount of organic compounds and contributes only 1% to the volume stream of municipal wastewaters. Nitrogen (N), phosphorus (P) and potassium (K) are an important food source for the growth of living organisms [Lind et al. 2000, Ganrot et al. 2008, Liu et al. 2008, Antonini et al. 2011, Luther et al. 2015]. Therefore, urine can be considered as a valuable source for the recovery of nutrients and also energy and numerous technologies have been developed to recover these nutrients. Human urine may be dangerous about hygienically if it mixed with feces. For this purpose, urine should be collected separately at source.

Source separation of urine can generate an ideal situation for nitrogen and phosphorus recovery, the load of the wastewater treatment plants and reduction of treatment costs. For that reasons, the urine-separating toilet can be used for collect urine separately from feces. Nutrients especially nitrogen and phosphorus can be recovered from human urine. On the other hand, removal of nutrients is very important issue because wastewater management because they cause eutrophication problem by discharging of wastewater with high nutrients (nitrogen and phosphorus) into aquatic media [Nancharaiah et al. 2016]. by microorganisms in which conventional methods, the mostly ammonium nitrogen is converted into harmless nitrogen gas and the phosphorus is consumed for requirements. However, volume reduction, phosphate recovery, nitrogen recovery, stabilization, hygiene, removal of micro contaminants and nutrient recovery is important in urine treatment. Therefore, new technologies are being developed for urine treatment and nutrient recovery. Electrochemical treatment is one of the widely used and still developing technologies [Radjenovic and Sedlak 2015].
The advantages of electrochemical treatment include high removal efficiency, favorable operating conditions, small equipment sizes, no secondary waste, no additional chemicals, transportation and storage not required, could be fully automatized and low capital and operational costs. These reasons put the electrochemical technologies into environmentally friendly technologies. The electrochemical processes take place from two electrons, one being the anode in which the oxidation reactions take place and the other being the cathode in which the reduction takes place. It is also possible to obtain energy from wastewater by means of cathodic reactions [Luther et al. 2015, Radjenovic and Sedlak 2015].

This paper has reviewed the nutrients removal from human urine and recovery in various electrochemical system and discussed the influence factors and potential problems, and identified the key challenges for nitrogen and phosphorus removal/recovery.

2. Results

Urine contains nitrogen, phosphorus and potassium that required for fertilizer production. Urine is an alternative source for nutrients. In addition to this, no mix toilets provide to separate collection of urine, resulting in increased wastewater quality and lightening of the wastewater treatment plants load. Electrochemical processes are becoming alternative technology for recovering ammonium from human urine. Electrochemical systems offer several benefits, such as less chemical use, easy to operate, sludge does not form after the process and to be installed in confined spaces.

This evaluation can be a source of information for existing and developing electrochemical systems and helps to select the process by demonstrating the advantages and disadvantages. Electrochemical processes appear to be a promising technology for nutrient recovery from human urine.

References

Evaluation of Energy Recovery Potential of a Small Water Distribution Network using a Pump as Turbine System: Antalya-Kaleici Case Study

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Keywords: energy recovery, excess pressure, pump as turbine, water distribution network.

Abstract

Energy recovery from excess water pressure in water distribution networks using pump as turbine (PAT) systems presents a viable option for reduction of water and energy losses besides greenhouse gas emissions. This study presents the initial findings of a feasibility study for a possible PAT application at Kaleici pilot study area in Antalya-Turkey. The average power production values were obtained as 0.71 and 1.32 kWh for peak season and off-season pressure reduction levels of 5 m and 9 m, respectively.

1. Introduction

Reducing water losses, energy losses and carbon dioxide emissions are among the primary goals for the implementation of sustainable water supply systems. Most of the water supply systems exhibit excess water pressure where break pressure tanks, reservoirs or pressure reducing valves are commonly used to reduce the excess pressure. Energy recovery from excess water pressure in water distribution networks (WDNs) is a new subject of interest. Excess pressure in WDNs causes excess water losses and frequent pipe breaks besides reducing the service life of the WDN. Saving water implies saving energy that is used to abstract, treat and pump the water to the WDN. In recent years, the use of PAT has attracted considerable interest for reducing excess pressure besides energy recovery. Recently, a full-scale PAT system was implemented and operated at Anfaş WDN of Antalya city within the scope of a research project (Muhammetoglu et al., 2017, 2018). With the implementation of this PAT system, excess pressure of approximately 1 bar have been reduced that led to considerable reduction in water losses besides an average power production of 2.37 kWh for an average flow rate of 165 m³/h. After this successful application of PAT system, an alternative pilot study area (PSA), Kaleici, was investigated for energy recovery potential using a PAT system and its initial findings were presented in this study.

2. Materials and Methods

Kaleici is a famous tourism destination located at the center of Antalya city. The topography is highly changing at Kaleici PSA where the elevations vary between 0 to 40 meters above the mean sea level (Figure 1) which causes excess water pressure mainly at the low elevations of the WDN. PSA is a single inlet district metered area (DMA) that is isolated from the rest of WDN of Antalya city. Flow rates and water pressures are continuously measured online at the SCADA station located at the entrance of the PSA in addition to five online pressure measurement points (PMP) within the WDN, located at different elevation levels (Figure 1). The US-EPA EPANET hydraulic model was applied to the PSA to obtain optimum operational pressure at the inlet of DMA and to determine excess water pressure
levels. The physical configuration of WDN and other relevant data sets required for EPANET model were obtained from Antalya Water and Wastewater Authority, ASAT.

![Figure 1. Water distribution network of Kaleici PSA and locations of SCADA station and pressure measurement points (Kara et al., 2016)](image)

3. Results

EPANET model was initially calibrated for Hazen-Williams pipe roughness coefficient and the predicted pressure values were in good agreement with field measurements. The excess water pressure heads were determined as 5 m for the peak season months (May, June, July, August, September and October) and 9 m for the off-season months (November, December, January, February, March and April). The average power production values were obtained as 0.71 and 1.32 kWh for peak season and off-season months, respectively whereas the flow rates passing through PAT system were determined as 87.58 and 88.75 m$^3$/h for peak season and off-season months, respectively. The temporal variations of flow rate passing through PAT system and the power production were presented at Figure 2 for January 2017. The average efficiency of PAT system was assumed as 60% based on the results obtained from Anfaş WDN. The potential energy recovery of Kaleici PSA was less than the full-scale application at Anfaş WDN due to low flow rates and low levels of pressure reduction at Kaleici PSA. Based on these initial findings, a cost-benefit analysis is required to evaluate the pay-back period of a possible PAT system implementation at Kaleici PSA and to help decision makers to give a final decision on its application.

![Figure 2. Temporal variations of flow rate passing through PAT system and power production for January 2017](image)
References


The Impact of Supplying Information and Awareness Raising on Public Attitude for Acceptance of Grey Water Reuse in Istanbul

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Keywords: Grey water management, reuse, public opinion/acceptance, public surveys, sustainability.

Abstract

Utilization of grey water as an alternative source of water is a recent useful option to serve environmental sustainability, especially in water stressed and water scarce areas. Public acceptance is one of the key determinants of the success of grey water reuse. Surveys conducted in the Turkish megacity Istanbul show that informing public about grey water and its management is a major factor in raising awareness and improving the level of acceptance.

1. Introduction

Segregation of domestic wastewater at the source is one of the best options for recycling and reuse of valuable materials embedded in domestic wastewater. Grey water is the stream which will result from such segregation regardless of the type of separation used. Containing all but toilet wastewater, grey water will consist of wastewater from a number of different washing functions in the households like bath tubs/showers, wash basins, laundries, kitchen sinks and dishwashers. As grey water constitutes 75% by volume and contains lesser amounts pollutants as compared to conventional domestic wastewater, reclamation and reuse of this renewable alternative source presents an obvious benefit. Although treating grey water for reuse as an alternative water source to almost any high quality demanding end use is technically possible, positive public opinion and acceptance by consumers is one of the key elements in success for full scale practice. Furthermore, positive opinion and acceptance necessitates awareness in the subject matter and must be based on sound information about grey water management.

This work was undertaken to investigate awareness and attitude of the public, and the impact of supplying information upon acceptance of grey water reuse. The paper will report the results of the survey conducted in the Turkish megacity Istanbul focusing on present awareness and willingness of participants to use reclaimed grey water along with changes in their perception and level of acceptance after being informed about the subject matter, mostly focusing on possible final uses, sources of grey water and economic considerations.

2. Materials and Methods

This preliminary survey of 30 questions was run in Istanbul, Turkey with 227 participants on a face to face basis to be able to supply information and to directly answer any questions that they may pose. After finishing the entire questionnaire, participants were supplied with a standard piece of information on grey water and nine of the questions were repeated for the second time to assess the effect of supplying information. Meanwhile, questions from the participants were answered. The assessment was mainly based on counts and percentages of possible choices. Changes in attitudes were calculated on based on the
percentage of the acceptances/options indicated in replies in the first (before) and second (after) rounds.

3. Results

The results have revealed that the awareness regarding grey water and its reuse was low and did not exceed 30% before information sharing. Grey water from handwash basins received the highest acceptance among five different sources in the household with 65% at the beginning but converged to the range 73-82% after being informed. In terms of possible end uses of reclaimed grey water, Table 1 summarizes acceptances and the change in attitudes of participants after being informed, to show that overall, the greatest acceptance as the final use was with toilet flushing with 79% acceptance which still remained as the highest with 92%. The lowest was uncooked vegetables with 25% and increased to 41%. Overall the highest increase was observed with laundries with a change of 83%. Economic considerations were observed to play an important role in public acceptance and participants said they would accept to pay for installation of grey water systems with 40% but would accept its installation for free with 79%, both of which have increased to 58 and 93%, respectively, after learning more about grey water management.

Table 1. Acceptances (as head counts) and changes in attitudes of participants after being informed about grey water reuse

<table>
<thead>
<tr>
<th>Final Use</th>
<th>Option Description</th>
<th>Before informing</th>
<th>After informing</th>
<th>% Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Household use</td>
<td>Toilet flushing</td>
<td>179</td>
<td>209</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>Car washing</td>
<td>158</td>
<td>193</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>Swimming pools</td>
<td>50</td>
<td>81</td>
<td>62</td>
</tr>
<tr>
<td>Irrigation - Agricultural</td>
<td>Cereals/grains</td>
<td>130</td>
<td>161</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>Nuts in shells</td>
<td>132</td>
<td>175</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>Fruits on soil</td>
<td>94</td>
<td>135</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>Fruits on trees</td>
<td>120</td>
<td>157</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>Cooked vegetables</td>
<td>95</td>
<td>116</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>Uncooked vegetables</td>
<td>57</td>
<td>93</td>
<td>63</td>
</tr>
<tr>
<td>Irrigation - Landscape</td>
<td>Home gardens</td>
<td>170</td>
<td>205</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>Picnic area</td>
<td>159</td>
<td>202</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>Landscape</td>
<td>162</td>
<td>197</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>Park</td>
<td>169</td>
<td>204</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>Stadium</td>
<td>143</td>
<td>183</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>Playground</td>
<td>166</td>
<td>196</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>School garden</td>
<td>153</td>
<td>184</td>
<td>20</td>
</tr>
<tr>
<td>Industrial/commercial</td>
<td>Mixing concrete</td>
<td>164</td>
<td>200</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>Industrial applications</td>
<td>166</td>
<td>200</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>Laundries</td>
<td>77</td>
<td>141</td>
<td>83</td>
</tr>
<tr>
<td>Urban/municipal</td>
<td>Fire fighting</td>
<td>177</td>
<td>208</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>Street cleaning</td>
<td>178</td>
<td>214</td>
<td>20</td>
</tr>
</tbody>
</table>

All in all, for all questions in the survey there was an increase in public acceptance ranging from 17 to 83% showing the positive impact of supplying information to the public in terms of enhancing willingness to reuse grey water.

References

Baseline Values of Greenhouse Gas Emissions for an Airport

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Keywords: airport, carbon footprint, greenhouse gasses, sustainable development.

Abstract

The air transport industry provides by far the fastest mode of transportation when compared with road and marine transport. With reference to the data of International Air Transport Association (IATA), global passenger traffic expressed as “revenue passenger km” (the product of the number of passengers and the distance they travelled) was raised by 5.9 % just within year. This growth in air travel is accompanied by negative environmental impacts such as increases in greenhouse gas emissions. On a global basis currently, the aviation sector is responsible for 2 % of all the anthropogenic CO₂ emissions. This percentage is estimated to increase up to about 15 % by the year 2050. Total greenhouse gas emissions of Turkey is about 486236 thousand tons in 2015. It is stated that plans will be developed to elevate the share and load factor of airways in Climate Change Strategy document of Turkey that covers 2010 to 2020. On the other hand, greenhouse gas emissions arising from international air transportation will be monitored according to Turkish Climate Change Action Plan. The environmental impacts of the aviation industry are not only due to aircraft operation, but also due to airport operations. Thus, environmentally sustainable airports must be considered as an inseparable part of sustainable aviation systems and future airport growth is stated to be mainly limited by environmental impacts. As such, enlargement plans for airports must also take into account their environmental footprint. In this context, the objective of this study is to assess the greenhouse gas emissions baseline for an existing airport, on which emission reduction strategies can then be established. For this purpose, Sabiha Gokcen International Airport, located on the Asian side of Istanbul is investigated. Approximately 1470530 tons of CO₂ equivalent (e) emissions are generated by this airport annually. Aircrafts, ground access to airport, waste disposal, energy usage, airside vehicles, de-icer usage and wastewater processing are the contributors considered for greenhouse gas emissions. As expected aircrafts have the highest share in total CO₂ e. Ground access to airport, indicating how to reach the airport by ground transportation vehicles for passengers, employees, cargo etc. accounts for 11 % of the total emissions. CO₂ emissions that originate from sources owned or controlled by the airport, are only 4 % of the total emissions mentioned. Nevertheless, airport operators must lower these emissions (de-icer usage, airside vehicles, waste disposal etc). by taking necessary precautions. Total CO₂ e emissions showed a 55 % increase within a three year period of time. On the other hand, within the same period, obtained figures show a slightly decreasing trend for kg CO₂ e emissions per passenger.

References

Assessment of Energy Efficiency in Wastewater Treatment

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Keywords: energy efficiency, energy positive wwtp, anammox, HRAS, CEPS

Abstract

In this study, the energy balance of novel wastewater treatment processes were calculated and compared with the energy demand of a full-scale conventional biological nutrient removal (BNR) plant in Istanbul, Turkey. Comparison was performed based on the aeration and internal recirculation pumping costs considering that they are the two major constituents of the operation cost of a sewage treatment plant. Chemically enhanced primary sedimentation (CEPS) and high rate activated sludge (HRAS) process followed by partial nitritation and Anammox (PN/A) were selected as novel alternative for conventional BNR process. Flowrate and influent wastewater characteristics of a full scale advanced wastewater treatment plant were used in energy calculations. Results showed that conventional BNR system has a net energy demand of 1535 kWh/day whereas CEPS-PN/A and HRAS-PN/A have net energy gain of 28110 kWh/day and 26454 kW/day, respectively.

1. Introduction

In recent years, there are many ongoing discussions about the existing conventional wastewater treatment plants having high energy consumption (carbon footprint), greenhouse gas emissions (CO₂, N₂O and CH₄) and pollution created with waste sludge (micropollutants). In many cases, changes made to improve the performance of the wastewater treatment plants results in more electricity consumption and greenhouse gas emissions. Along with increased energy demand, efforts are being made to operate the wastewater treatment plants with lower energy consumption or in an energy-neutral, even energy-positive sustainable way. Transition to energy-neutral or energy-positive treatment plants brings the “net energy balance term” with it. This term means the energy conservation / savings for plants. As a first step, energy consumption points and the amount of energy consumption should be determined. Then the energy production possibilities should be evaluated. In addition to reducing energy consumption for energy-neutral or energy-positive domestic wastewater treatment plants, it is also essential to increase the amount of energy produced.

The most efficient way to reduce energy consumption is by reducing the aeration needed for both conventional carbon, nitrogen and phosphorus removal through aerobic process (aerobic degradation, nitrification etc.) process in the main stream. Aeration requirement could minimized by separating organic matter ahead of nitrogen removal stage by the use of as little (or no) air as possible and by implementing de-ammonification (partial nitritation/anammox) instead of nitrification/ denitrification processes for N-removal (Shi, C.Y., (2011). There is no doubt that the most efficient way to produce energy (as biogas) is by anaerobic digestion of the sludge. Compared to the conventional treatment, biogas
production may be enhanced by producing a sludge with a high biogas potential or by increasing biodegradability of the sludge through some pretreatments.

2. Materials and Methods

Energy balance calculations carried out for three different treatment plant configurations; 1) conventional PC+conventional BNR+anaerobic digestion 2) CEPS+PN/A+AD and 3) HrAS+PN/A+AD. Flowrate and influent wastewater characteristics of the full-scale advanced wastewater treatment plant were used in energy calculations (Table 1). Metcald & Eddy approach used in sludge production, air requirement etc. (Metcalf & Eddy, 2003).

3. Results

The results of the energy balance calculations are given in Figure 1. Energy gain from CEPS+PN/A and HRAS+PN/A are almost same. CEPS+PN/A alternative requires use of a coagulant for the removal of organics from wastewater. Besides increased operational cost of using a chemical, phosphorus removal takes place along with the organics. If phosphorus recovery is an option, operational costs related to phosphorus extraction from the chemical sludge increases. On the other hand, there is insignificant phosphorus removal in the HRAS+PN/A option which give an opportunity recover phosphorus as CaPO$_4$ form from the treated effluent. A second important point that should be considered in the case of CEPS+PN/A option is the decrease of the anaerobic digestion efficiency if alum is used as a coagulant for the removal of organics from the influent. In this regard, FeCl$_3$ come forward as a promising alternative since it does not affect the digestion performance.

Table 1. Wastewater characterization of the treatment plant used in the energy balance calculations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Flowrate, m$^3$/day</th>
<th>Temperature, °C</th>
<th>COD, mg/L</th>
<th>BOD, mg/L</th>
<th>SS, mg/L</th>
<th>TKN, mg/L</th>
<th>TP, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flowrate</td>
<td>170000</td>
<td>16</td>
<td>513</td>
<td>292</td>
<td>350</td>
<td>59</td>
<td>6.25</td>
</tr>
</tbody>
</table>

Figure 1. Comparison of the energy balances for different wastewater treatment configurations

References


Which Effluent Quality for Which Reuse in the Mediterranean Region?

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Keywords: Sanitation, sewerage, effluent standards, wastewater treatment

Abstract

The structural water stress dominating in the Mediterranean Region and Middle East, is increasingly felt in the face of climate change impacts. These impacts coupled with demographic pressure on water resources are expected to be an unprecedented obstacle to the Sustainable Development Goals (SDGs), and the 6th objective, in particular “ensuring access to water and sanitation for all and ensuring the sustainable management of water resources”. Furthermore, these impacts may also hinder the resolutions of the Paris Agreement. All these unfavourable conditions make the Mediterranean Region, one of the most vulnerable areas of the World where 60% of the world’s population has hardly 1000m³ water /per capita-year. Therefore, a sound water accounting that enables estimating all fresh conventional water resources together with unconventional water resources will be a basis for future planning. Accordingly, the volume of wastewater produced in Southern and Eastern Mediterranean Countries (SEMCs) was estimated at 8,134 km³ (with the exception of Israel) which makes it a valuable source with regard to its quantity. In order to reuse wastewater, the first requirement is to have access to sewerage network connected to wastewater treatment plants (WWTPs) (IPEMED 2018). According to the World Bank records, Mediterranean populations are having improved access to sanitation services with about 90% for SEMCs and 97% for Mediterranean countries in 2015. However, these figures do not mean that there is available treated effluent for reuse. The situation is complex with regard to efficient interception of the sewage and treatment. Although in coastal urban area, sewerage network is satisfactory, in general, inland less developed settlements have poor sanitation networks, with often leaking septic tanks, combined sewer system with overflow structure, illegal connection to streams etc. Also, reuse can be implemented in case satisfactory sanitation scheme is in place, i.e. sewerage, treatment plant and network for reuse complying with the corresponding standards. Since any effluent quality does not match with the required reuse, the question of “which effluent quality for which reuse” is a prerequisite in this instance.

All these negative impacts result in loss of wastewater which becomes, de facto, a loss for circular economy and threat for environmental pollution. The combined conclusion is that wastewater which must be considered as a resource remains little exploited in the Mediterranean region.

Introduction

Main challenges for reuse in Mediterranean cities are;

- Mediterranean cities have congested population
- Land is expensive in coastal cities where competing sectoral use is a big challenge
No room for extension of existing uwwtp (urban waste water treatment plants)
Uwwtp in coastal cities have been designed with sea outfall after primary treatment (e.g. Istanbul case) no room for improved treatment
Central uwwtp or individual for each agglomeration?
Compact plants, how?

Figure 1. Sectors in which (tertiary) treated waste water can be reused (IPEMED 2018)

2. Materials and Methods

In this paper, a detailed analysis for potential reuse in the selected region/countries is done with a comparison of corresponding standards for different reuses. The replicability of each reuse Project is investigated.

“Appointed as coordinators of the working group on the “urban” topic, the Economic Foresight Institute for the Mediterranean World (IPEMED) and the Medcities network wished to take advantage of this process to highlight the know-how of cities and operators in terms of reuse of treated waste water (REUSE); as this topic was the main subject of the last United Nations report on the development of water resources”(IPEMED 2018)

The following questions are debated through case studies implemented in Jordan, Egypt, Tunisia, France and Turkey, respectively.

- Which quality of tww (treated waste water) for which reuse?
- Which challenges
- Which drivers?

3. Results

The results of the case studies show that water stress countries make good use of tww «not one drop can be wasted!» (e.g. Israel, Spain, SEMC). Which drivers can encourage decision-makers, policy-makers, users, operators to use tww in non water-stressed regions / countries?

- Environmental-friendly approach? Acceptance by the users?
- Circular economy?
- Economic approach? Pricing?
- Is it worth using tww in water-rich regions?

References

FAO - AQUASTAT data: www.fao.org/NR/WATER/AQUASTAT/main/indexfra.stm
Influences of Microwave, MW/H₂O₂ and MW/S₂O₈²⁻ Pre-treatments on the BMP Potential of the Wastewater Sludges

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Keywords: BMP, microwave pre-treatment, persulfate pre-treatment, hydrogen peroxide pre-treatment, anaerobic digestion.

Abstract

The wastewater sludge stabilization with the application of various pre-treatments is sufficient to reduce the organic content of the sludge and to produce energy. Anaerobic digestion (AD) has been used to stabilize wastewater sludges while producing biogas energy. Efficiency of digestion and methane production can be enhanced by pre-treating the sludge prior to AD. This study investigates the effects of microwave (MW), combined microwave-hydrogen peroxide (MW/H₂O₂) and combined microwave-persulfate (MW/S₂O₈²⁻) pre-treatments on the biochemical methane production (BMP) potential of wastewater sludges.

In the study, microwave pretreatment was applied to sludge samples at 160°C for 15 minutes in a MW oven. The MW/H₂O₂ and the MW/S₂O₈²⁻ pretreatments were applied to sludge samples by mixing them with 1 g H₂O₂/g TS and 1 g S₂O₈²⁻/g TS, and then microwaving them. The inoculum and the pretreated sludge samples were mixed in 120 mL reactors with an inoculum to substrate ratio (I:S) of 1:1 (w/w on VS basis). The reactors were sealed and flushed with nitrogen gas for 2 minutes to create an anaerobic environment. All reactors were anaerobically digested at 37°C for 40 days. Total gas productions were measured daily and gas compositions were analyzed weekly during the digestion period of the batch reactors. Initial and final characteristics of the reactor contents were analyzed according to Standard Methods.

The MW and MW/H₂O₂ pre-treatments speeded up the hydrolysis step and improved the biodegradability of the organics by increasing their solubility. Application of MW and combined MW/H₂O₂ pre-treatments prior to AD increased the methane yields by 64% and 38%. The MW/S₂O₈²⁻ pre-treatment also improved the biodegradability of the organics, but unfortunately 1 g/g TS concentration of S₂O₈²⁻ created an inhibitory effect on the methanogens and so methane production cannot be achieved.
Electro-Fenton treatment of Naphtol Blue Black dye by using synthesized Dawson-type heteropolyanions as catalyst

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**Keywords**: Electro-Fenton, NBB, Carbon-felt, Textile, Synthetic wastewater, Mineralization

**Abstract**

Textile industry is producing highly toxic wastewater and treatment of it becomes a major social concern to protect the environment. The dye wastewaters include various chemical substances, especially dyes, resistant to biodegradation and they are suspected to cause mutation of non-target organisms and ecology. This study examines the degradation and removal of Naphtol Blue Black (NBB), in aqueous medium by using electro-Fenton process. NBB is a textile diazo dye has been identified in water bodies even after some advanced oxidation treatment of the effluent wastewater [1, 2]. TiO\textsubscript{2} is generally used as heterogeneous catalyst to degrade NBB [3, 4]. Because NBB is hard-to-remove by conventional treatment techniques, the advanced treatment is necessary. Electrochemical oxidation methods have been applied. In this study, NBB has been degraded and discolored by using synthesized Dawson-type heteropolyanions as catalyst in electro-Fenton process [5, 6].

Dawson-type heteropolyanions are formidable catalysts, which have proved their effectiveness in many reactions of oxidation [7-9]. Dawson-type heteropolyanions constitute an interesting generation of selective and recyclable catalysts [9].

According to the results obtained, the use of Dawson-type heteropolyanions as catalyst was shown to have beneficial effect on the removal of NBB. The treatment efficiency was followed by total organic carbon (TOC) and high performance liquid chromatography (HPLC). 0.1 mM NBB solution was treated in a current range of 50 – 300 mA. The best degradation efficiency was reached at 15 min at 100 mA (99.9\% NBB degradation). In contrast, the better mineralization rate (70\% in terms of TOC removal) was obtained at 300 mA after 6 h treatment. Additionally, the ions (i.e. NO\textsubscript{3}\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-} and NH\textsubscript{4}\textsuperscript{+}) released to the solution during mineralization process were analyzed; their concentrations were increasing along the treatment time. These results highlight that the electro-Fenton process using Dawson-type heteropolyanions as catalysts is applicable efficiently to removal NBB from textile wastewater.

**References**

Removal of Micropollutants by Membrane Distillation Bioreactor

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Keywords: Membrane distillation bioreactor, thermophilic, micropollutants, treatment wastewater

Abstract

The removal of micropollutants (MPs) by a novel thermophilic membrane distillation bioreactor (MDBR) system was examined. A bench scale MDBR system with flat sheet membrane was used in this study. The results showed that biodegradation, sludge adsorption, and rejection by MD enhanced in the removal of MPs in hospital wastewater and effluent quality of MDBR. An equilibrium flux of 4.33L/m²·h for more than a month without membrane cleaning was achieved.

1. Introduction

Increase in concentration of micropollutants in surface waters and ground waters has attracted consideration in recent years. MPs consist of pollutants such as surfactant, pharmaceuticals and personal care products, endocrine disruptors, unregistered drugs, gasoline additive pollutants. Among these pollutants, consumption of pharmaceutical has been increasing every passing year. After use of these drugs, only to a certain portion is metabolized. Non-metabolized portion is usually excreted from the body through urine. Hospital wastewater, one of the important source of these pollutants, consist of recalcitrant and toxic MPs originating from drug metabolites, products, chemicals, heavy metals, disinfectants and sterilizing of endoscopy and other devices specific detergents, radioactive tracers and iodine contrast solution (ICM).

Membrane bioreactors (MBRs) integrate low pressure membrane filtration, such as microfiltration (MF) or ultrafiltration (UF), with activated sludge treatment. In recent decades, it has been seen that the maturity of MBR systems, as an alternative wastewater treatment technology, is superior than the conventional activated sludge (CAS) treatment processes. MBRs integrate low pressure membrane filtration, such as microfiltration (MF) or ultrafiltration (UF), with activated sludge treatment. Compared to CAS processes, MBRs are usually operated at higher biomass concentrations (i.e. 10-20 g/L) and longer sludge retention times (i.e. 10-30 d), resulting in better quality effluent and lower sludge production. For the same treatment capacity, the physical footprint of MBR is also much smaller than that of the CAS process.

In term of treatment of MPs, hydrophobic MPs can adsorb to the biosolids, resulting in longer retention times in the MBR, and thereby exhibiting higher removal efficiency than the CAS process. However, some hydrophilic MPs such as carbamazepine and diclofenac can be similarly persistent to CAS and MBR treatment. Because MPs can freely permeate through MF and UF membranes, the retention time of the hydrophilic and persistent MPs in the bioreactor is the same as the hydraulic retention time (HRT). Thus, the occurrence of hydrophilic and persistent MPs in MBR permeate necessitates a post-treatment process to ensure their removal if water reuse is intended. The post-treatment process mainly involves reverse osmosis or nanofiltration, UV oxidation or ozonation. While high water quality is
achieved after these multiple treatment processes, they can be expensive, energy intensive and, thus can compromise the economics and environmental disadvantages of water reuse.

MDBR is a novel technology that combines a bioreactor for wastewater treatment with membrane distillation. MD several benefits including 100% (theoretical) rejection of ions, macro-molecules, colloids, cells and other non-volatiles; lower operating temperatures than conventional distillations; lower operating pressures than conventional pressure-driven membrane separation processes and so forth. The membranes used in MDBR are microporous and hydrophobic.

2. Materials and Methods

The MDBR system, used in this study, is presented in Figure 1. The temperature in the reactor is 55.5±1°C and filtrates temperature, in other side of membrane, is hold fixed in 19.5±2°C. Effective volume of the reactor has 5 L and direct contact module has 220 cm² area. Hydrophobic PVDF membrane, with pore diameter 0.2 µm is used as distillation membrane.

![Figure 1](image)

Figure 1. Schematic of MDBR (1. Reactor with jacket, 2. module of membrane distillation, 3. peristaltic pump, 4. supply tank, 5. balance, 6. filtrate collecting tank, 7. refrigerator, 8. computer (for control and automatisation management), 9. blower.)

3. Results

The molecular weight of MPs detected in this study, 176 g/mol (cotinine) to 1350 g/mol (virginiamycin) ranged. There is no correlation between the removal efficiency and molecular weights of these micropollutants. However, the results show that the removal efficiencies are quite high and even some micropollutants are completely removed. For example, caffeine was treated with a very high removal efficiency, average 88%, in MDBR. It was possible that the micropollutant may pass into the volatile form due to its pKH value of less than 9. It is also hydrophilic because log D value is lower than 3.2. Considering, its pKH and log D, the removal mechanism of this micropollutant was biodegradation and transformation without adsorbing to the sludge (Wijekoon et al., 2013). As for flux of the MDBR, the initial flux in MDBR is 7.85 L/m²·h and the equilibrium flux is 4.33 L/m²·h. The fouling layer on the membrane led to decrease in the flux in two ways which were: reducing vapor pressure on the membrane surface (Gryta, 2008) depending on heat insulation properties of fouling layer and reducing mass transfer resulting of some nonporous fouling layer (Khaing et al., 2010). Finally, the distillate conductivity was 1.00 µS/cm at the beginning and 105.00 µS/cm at the end of 20 days.
Acknowledgments

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References


Wastewater Treatment in Anoxic/Oxic- Membrane Bioreactor (A2O-MBR) by Assisted Ionizing Radiation

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e Keywords: anoxic/oxic membrane bioreactor, ionizing radiation, coking wastewater, treatment

Abstract

The treatment of coking wastewater by a A2O-MBR by assisted ionizing radiation hybrid system was examined. The wastewater was irradiated at different absorbed doses by Co-60 gamma rays, leading to both oxidizing and reducing radicals, before it given to the A2O-MBR operated at 35±2°C for treatment of carbon and nitrogen simultaneously. A hollow fiber PES membrane module with a pore diameter of 0.2 μm and a membrane area of 0.2 m² was used in the oxic reactor. Membrane was operated at constant flow and had automatic backwash system. The results showed that the gamma ionizing radiation has also reduced the toxic effect of coking wastewater on activated sludge, resulting from degradation of toxic pollutants such as cyanide, thiocyanate and phenol.

1. Introduction

Increased public awareness of environmental pollution and tightening of environmental laws have led to the development of environment-centered technologies in many countries. Since some surfactants and pollutants such as lignin and pesticides, cannot been biodegraded by conventional biochemical methods, they escape from treatment plants. The rate and ratio of biodegradation of pollutants in wastewater depend on the nature of the pollutants and their oxidation levels. Pre-oxidations of recalcitrant molecules increase their biodegradability. Systematic investigations have shown that pre-oxidation of recalcitrant pollutants by ionizing radiation is one of the most promising techniques prior to biodegradation.

Research and development studies of treatment of industrial wastewater using ionizing radiation are being made in many countries such as USA, Canada, Russia, Italy, Brazil, China, South Korea, Austria, Japan, Indonesia, Egypt, Ghana, Cuba and Turkey. The studies include various wastewaters such as the paper industry, paint industry, textile-paint industry, synthetic rubber plant wastewaters. As a result of these studies, the biodegradability of recalcitrant organic pollutants has increased significantly after oxidation with ionizing radiation (Chmielewski, 2007). Hence, hybrid systems formed by the use of ionizing radiation together with other treatment methods have begun to attract attention (Pikaev, 1999).

2. Material and Methods

The aim of this study is to increase the biodegradability of the iron-steel industry coke wastewater, containing toxic, inhibitor and recalcitrant organic pollutants, by using gamma rays and after then to treatability of the irradiated wastewater in A2O-MBR system. The
wastewater was irradiated at different absorbed doses by Co-60 gamma rays, leading to both oxidizing and reducing radicals, before it given to the A2O-MBR operated at 35±2°C for treatment of carbon and nitrogen simultaneously. The effective volume of the anoxic and oxic reactors used in the study is 8 L and 16 L, respectively. A hollow fiber PES membrane module with a pore diameter of 0.2 μm and a membrane area of 0.2 m² was used in the oxic reactor. Membrane was operated at constant flow and had automatic backwash system. The filtrate from the membrane was used in the backwash. Air is supplied from the air compressor. The schematic representation of the system is presented in Figure 1.

![Schematic Representation](image)

**Figure 1.** A2O-MBR system, 1- feed tank, 2- anoxic reactor, 3- oxic reactor, 4- peristaltic pump (for wastewater feed), 5- mixer, 6- peristaltic pump (for recirculation), 7- membrane module, 8- Na₂CO₃ dosing pump, 9- Na₂CO₃ reservoir, 10- vacuum pump (to obtain membrane filtrate), 11- air compressor, 12- balance, 13- computer (for control and automation)

### 3. Results

System performance is evaluated in terms of ammonia, nitrate, phenol, thiocyanate, total cyanide as well as conventional treatment parameters. The gamma ionizing radiation has also reduced the toxic effect of coking wastewater on activated sludge, as it degraded toxic compounds such as cyanide, thiocyanate and phenol. It was observed that the BOD was completely removed in the samples taken from the effluent of the A2O-MBR system. It was also found that the nitrate concentration was reduced to 2 mg/L, while the ammonia was completely removed.

### Acknowledgements

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Comparison of Aspen Modeling System Results to Performed Gasification Experiments

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Keywords: Aspen Plus, gasification, modelling, waste-to-energy.

Abstract

The purpose of this study is to determine the compatibility of the results of the gasification experiments made with the laboratory scale to the results of the gasification model which was created using the Aspen Plus software program working on the principle of thermodynamic equilibrium principle and operated under the same conditions as the laboratory conditions. In the study, the results obtained from laboratory-scale experiments were compared with the modeled results. The operating parameters in the experiments under laboratory conditions and the operating parameters in the Aspen Plus computer aided modeling program were in agreement. It has been found that the synthesis gas values produced in this harmony vary. It is predicted that this is caused by differences in model assumptions, such as program assumptions and reactor type. It has been concluded that the use of Aspen Plus in engineering applications can shed light on further work.

1. Introduction

The concepts of waste management and energy recovery come to the forefront in today's conditions where the importance of energy is increasing. Under the conditions that the energy resources are exhausted and the waste is produced to a large extent, energy recovery from waste is a very important research area and a sector as a whole. Among the energy recovery methods, the notable gasification process is the controlled partial oxidation of the carbonaceous solid material, which is obtained by providing less oxygen than the stoichiometric requirement for complete combustion (Öngen and Arayıcı, 2015; Öngen et al., 2016).

With the Aspen program, a process simulation program, it is quite possible to do chemical process simulation for steady-state condition, and all kinds of information can be obtained with 23,000 pure substances, 30,000 binary mixtures and more than 4 million total experimental data in the database. Since the experimental studies take a lot of time and their costs are high, the studies on the gasification process through the models formed by experimental data are increasing day by day. Aspen Plus is widely used by researchers and commercial companies in the design of gasification processes. Established affinity models do not provide coincidental results with real systems, but when system inputs and reactions overlap thermodynamic and hydrodynamic conditions with real systems, the results obtained approach real systems (URL1).

The purpose of this study is to determine the compatibility of the results of the gasification experiments made with the laboratory scale to the results of the gasification model which was created using the Aspen Plus software program working on the principle of
thermodynamic equilibrium principle and operated under the same conditions as the laboratory conditions. Within the scope of the study, the results obtained from laboratory-scale experiments were compared with the modeled results. The compatibility of the operating parameters in experiments under laboratory conditions and the operating parameters in Aspen Plus computer aided modeling program has been examined.

2. Materials and Methods

For the laboratory studies, two organic substances were chosen, one being pomace and the other one being chicken manure. In the gasification experiments, an upflow, fixed bearing steel reactor with circulation with the cyclone unit was used. The warm-up speed of the system can be controlled instantaneously, but can’t be adjusted to different speeds. The design of the reactor assembly is given in Figure 1.

![Figure 1: Reactor design.](image)

Gasification experiments were carried out at 750°C under 1 bar pressure with 3 L / hour dry air agent. The gasification model was also run in the Aspen Plus program using the operating conditions in the laboratory. In the assumption made in the gasification model established in this study; it is assumed that the process is stable, isothermal, dimensionless, does not lose pressure and heat, does not form tar, does not have reactive or catalytic effect on the
bearing material used and the ash in the fuel. Drying and pyrolysis stages are instantaneous. It has been found that the air used in the system is composed of 21% O₂ and 79% N₂ gas and the pure oxygen used is composed of 100% O₂ gas. It is assumed that the temperature and pressure distribution are homogeneous, as long as the system is not changed, with constant temperature (750°C) and pressure (1 bar). Gibbs reactor was chosen as reactor, Peng-Robinson method was used. According to the elemental analysis of the fuel used, it is assumed to be H₂, O₂, N₂, H₂O, S, C and ash. It has been assumed that 0.01 kg / h of feed fuel is supplied to the system during the gasification process. It is assumed that only carbon is present in the solid phase in the gasifier. The model created in Aspen Plus computer aided modeling program is given in Figure 2.

3. Results

Gasification reactors containing chicken pest and pine waste were gasified at 750°C temperature, 1 bar pressure, 3 L / hour air condition. In the Aspen Plus modeling program, the gasification model was run at 750°C temperature, 1 bar pressure and 3 L / hour air conditions in order to see the compatibility / differences for model gasification and laboratory gasification. With its graphical charts for its two wastes. Figure X shows gas volume fractions and calorific value parameters for Aspen modeling and laboratory gasification for chicken manure and pomace.

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**Figure 2:** Aspen Plus computer aided modeling program based on laboratory conditions.
Looking at Figure 3, it can be seen that the results modeled in the Aspen Plus simulation program and the results of the gasification systems run in the laboratory show differences between gas volume percentages and thermal values. For both samples, the volumetric percentages of CO and H₂ gas are higher in the Aspen Plus modeling gasification. There are differences between laboratory results and Aspen Plus modeling gasification.

When the results of the model and the results of the laboratory were compared, significant differences were determined. Presence of limiting factors is foreseen for these differences. The laboratory scale gasification reactor shows little similarity with the Gibbs gasification reactor used in the technological and thermodynamical Aspen Plus software, and as a result of the assumptions made during the modeling, many parameters in real terms are overlooked by software as the most important limiting factors.

As a result, computer-aided approaches are frequently used in the design and prediction stages of many engineering models and real-scale systems. With the advantages of comparatively simulating many different variables and achieving the technical values with thermodynamic approaches, it has been concluded that the use of software in engineering applications will also be able to shed light on further studies.

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Development of a Model of Biomass Gasification by Aspen Plus

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Keywords: Aspen Plus, gasification, modelling.

Abstract

The purpose of this work is to determine the optimal gasification conditions for different waste types under different operating conditions with the Aspen Plus software program working on the principle of thermodynamic equilibrium principle. In the study, the rich gas forms which constitute the contents of the produced synthesis gas and the thermal value were observed and the most suitable operating conditions were determined to increase the production of hydrogen gas. Under optimum operating conditions, the hydrogen content of the synthesis gas reached about 60\% volumetric and the thermal value reached about 3000 kcal/m\textsuperscript{3}. With the advantages of comparatively simulating many different variables and achieving the technical values with thermodynamic approaches, it has been concluded that the use of software in engineering applications will also be able to shed light on further studies.

1. Introduction

With the increase in energy consumption, the demand for energy is increasing and searching for new energy sources is going on. Thermal processes are gaining value as methods that are rapidly increasing in applications and technologies developed all over the world. Among the thermal process technologies, the gasification process stands out as a clean and environmentally friendly technology with the lowest emission values and the least amount of waste generation. Computer aided modeling programs such as Aspen Plus have been used for years to obtain maximum efficiency in thermal processes (Öngen and Arayıcı, 2015; Öngen, 2016, URL1).

The purpose of this work is to determine the optimal gasification conditions for different waste types under different operating conditions with the Aspen Plus software program working on the principle of thermodynamic equilibrium principle. In the study, the rich gas forms which constitute the contents of the produced synthesis gas and the thermal value were observed and the most suitable operating conditions were determined to increase the production of hydrogen gas. Within the scope of the study, experiments were carried out on the gasification model under variable parameters of temperature and pressure of different wastes. According to the results obtained, optimum gasification conditions were determined under different operating conditions.

2. Materials and Methods

In the study, three wastes were selected: a mixture of 50\%:50\% of chicken manure-pomace, chicken manure and pomace. The gasification model designed using Aspen Plus computer aided modeling program consists of fuel supply, fuel separation, gasification, cooling, ash
separation and ammonia separation units. In the assumptions made in the gasification model established in the study; it is assumed that the process is stable, isothermal, dimensionless, does not lose pressure and heat, does not form tar, does not have reactive or catalytic effect on the bearing material used and the ash in the fuel. Drying and pyrolysis stages are instantaneous. It has been found that the air used in the system is composed of 21% O₂ and 79% N₂ gas and the pure oxygen used is composed of 100% O₂ gas. It is assumed that the temperature and pressure distribution in the system is homogeneous. Gibbs reactor was chosen as reactor, Peng-Robinson method was used. According to the elemental analysis of the fuel used, it is assumed to be H₂, O₂, N₂, H₂O, S, C and ash. It is assumed that only carbon is present in the solid phase in the gasifier. The model created in Aspen Plus computer aided modeling program is given in Figure 1.

Experiments were carried out in the study on the gasification model according to the variable parameters of chicken manure, pomace and chicken manure- pomace mixture wastes with temperature and pressure, and the results of the experiment are given graphically in the results section.

3. Results

The purpose of this work is to determine the optimal gasification conditions for different waste types under different operating conditions with the Aspen Plus software program working on the principle of thermodynamic equilibrium principle. In the study, experiments were made on the gasification model according to the variable parameters of chicken manure, pomace and chicken manure- pomace mixed wastes with temperature and pressure, and the results of the experiment are given graphically.
In the study, the effect of the change in temperature on the volumetric percentages of CH₄, H₂, and CO gases and the thermal value, operating at a temperature range of 700 to 1100°C, is given in Figure 2.

Referring to Figure 2, the volumetric percentages of CH₄, H₂, and CO gases increase with temperature increase. It is seen that the volume percentage of hydrogen gas increases by 55%, carbon monoxide increases by 45% and methane gas increases by 15%. When the effect of the temperature change on the thermal value and the volume percentage of the H₂ gas is considered, it is seen that the thermal value and the volumetric percentage of the hydrogen gas increase with the temperature increase. With the increase in temperature, the volume percentage of hydrogen gas reached 55% and the thermal value reached 3000 kcal / m³.

The effect of the pressure change on the volumetric percentages of the CH₄, H₂ and CO gases and on the thermal value is shown in Figure 3, in which the pressure was varied between 1 and 10 bar.
Referring to Fig. 3, when the pressure increased from 1 to 10 bara, the volumetric percentages of gas decreased. The increase in pressure has been a negative effect on the volumetric percentages of gas. When working at an optimum of 1 bar, all three gases had the highest gas volume percentages. When the effect of the pressure change on the thermal value and on the volumetric percentage of H₂ gas is considered, the volumetric percentage of the gases and the thermal value decrease with the pressure increase. The optimum volume of 1 bar H₂ gas has a volume percentage of 60% and a thermal value of 3000 kcal / m³.

As a result, it has been concluded that the use of software in engineering applications will also shed light on the progressive workings, such as the ability to simulate many different variables in a comparative manner and to achieve technical values through thermodynamic approaches.

References

URL1: https://www.aspentech.com/
Scaling and Biofouling as Limiting Factors for Membrane Treatment of Wastewater

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Keywords: Membranes, wastewater, scaling, fouling, biofouling

Abstract

Membrane techniques are widely used e.g. for water and wastewater treatment. However, scaling and fouling can significantly reduce life time and service time of the membranes, thus increasing the expenses of the treatment. Microbiological and molecular techniques are helpful tools to get more insight into the biofilm structure and function as a prerequisite to reduce fouling and biofouling processes.

1. Introduction

Today, between 1.4 and 2.1 billion people live in water-stressed areas around the world. 3.2 billion people may face water stress by 2100. Thus, new energy- and cost-efficient wastewater treatment technologies are vital for a sustainable development. As agriculture is the main water consumer in many countries, accounting for around 33% of average water use, the reuse of treated waste water in agriculture could be one way to overcome the increasing water scarity. Reuse of appropriately treated sewage offers an important source for irrigation as it is a potential nutrient source for crops and reduces fresh water demand. On the other hand, several contaminants, such as pharmaceutical products and their metabolites, personal care products, household chemicals, food additives and pathogens may be present in secondary treated sewage. All these contaminants may pose a risk in the food chain. Membrane techniques could be an efficient and low cost technique to eliminate these contaminants allmost completely. Beside wastewater and sewage treatment, membrane techniques are also used e.g. for the separation of pharmaceutical chemicals, for desalination of sea water and in water softening units. A new application is the conversion of solar energy into hydrogen for storage.

Crucial technical and cost factors in membrane techniques are total live time and sevice life of the membranes. Scaling, chemical fouling and biofouling are the dominant factors that significantly reduce service life and life time. Preventing or at least reducing scaling and fouling are therefore chalanges also for research and development.

2. Methods for biofilm characterization

During the last years, several new techniques offer a new insight into biofilm development and structures. As shown in several studies also in our lab, the surface structures of support and microorganisms are crucial factors in biofilm formation. According to the DLVO-theory, the surface free energy of interaction drives the primary adhesion of individual bacteria to the surface. Thereafter, surface free energy is also controlling the further biofilm formation. Fig. 1 shows an example for the biofilm development at different surfaces.
The primary adhering species do also control structure and composition of the growing biofilm. Unfortunately, many bacteria are also able to form a so called conditioning film, a small layer out of extracellular slime (sugar polymers, proteins but also extracellular DNA filaments) altering the surface properties of the carrier thus overcoming the limitation of surface free energy.

Several techniques are available to study biofilm formation and composition. The simplest one is Live/Dead staining combined with either optical fluorescence or laser scanning microscopy. This technique provide an insight into the overall biofilm structure. Additional techniques such as CTC staining visualize selectively viable and active living cells. Combining these techniques with in situ-fluorescence hybridization (Fish) offers the possibility to identify individual species within the biofilm. Additional staining techniques such as fluorescent lectin and Calcofluor white staining for extracellular sugar polymers and FITC for proteins and amino sugars give an overview to the structure of the extracellular matrix.

The surface characteristics of individual strains is measured e.g. by zeta potential measurement, micro titration, isoelectric focusing and others. However, the simplest technique to get information about adsorbtion to surfaces is the use of carrier materials containing defined surface structures.

3. Factors influencing biofilm formation and measures for preventing the formation of biofilms

Different efforts have been done to prevent or reduce the biofilm formation. This includes variation of surface flow, reduction of zones with low turbulence, variation of pH and addition of antiscalings and chemical bactericides. Newest developments try to implement antibacterial properties to the membrane itself. This includes modifications of the membrane to increase surface free energy of interaction or addition of antibacterial additives (e.g. Nano silver). One alternative to the addition of antimicrobial substances is the implementation of antimicrobial structures into the membrane-polymer. This prevents the loss of the antimicrobial additives. However, biofilm bacteria are able to adapt to environmental stress. Thus, they are also able to overcome antimicrobial measures. A more comprehensive insight into the biofilm structure and formation is therefore a prerequisite to reduce fouling processes.
Treatment of Microplastics

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Keywords: Microplastic, wastewater, treatment

Abstract

Microplastic particles are primarily made of polyethylene, polypropylene and other polymers. They have a structure smaller than 5 mm. As the production and use of plastics increased steadily over the decades, the appearance of microplastics in the environment has also increased in the same way. These new pollutants are now widely in all waters. Some researchers have focused on the removal of microplastics in wastewater treatment plants. The aim of this study is to draw attention to the importance of microplastics by gathering the studies on microplastic treatment.

1. Introduction

Microplastics are new anthropogenic pollutants found in different aquatic environments, including oceans, rivers, lakes and estuaries, as well as at the effluent of urban sewage and wastewater (Eerkes-Medrano et al., 2015). Microplastics are plastics smaller than 5 mm resulting from the decomposition of larger plastics that may cause adverse effects on organisms and ecosystems. (Van Cauwenberghe et al., 2015). Microplastics can also be a potential threat to human health by feeding on contaminated seafood. (Miranda and de Carvalho-Souza, 2016; Rochman et al., 2015).

Microplastics are more abundant in wastewater. Literature is lacking and not well known. Only a few researchers have carefully interested in removing microplastics from wastewater treatment plants (Carr et al., 2016; Mintenig et al., 2017; Murphy et al., 2016; Talvitie et al., 2017a). Furthermore treatment of microplastics with different methods are researched (Talvitie et al., 2017b). In this context, the aim of this study was reviewed to investigate the efficiency of process to remove microplastics from wastewater.

2. Materials and Methods

Scientific studies in the literature have been examined. In the paper, findings of these studies are included.

3. Results

Work in different areas of the world showed that most microplastics are removed during the primary treatment in wastewater treatment plants while secondary treatment is responsible for less in concentration. Despite a removal rate of 98% with a secondary WWTP in Scotland, it is estimated that 6.5x10^7 microplastics per day could enter the aquatic environment (Murphy et al. 2016). Moreover Carr et al. (2016) found that secondary treatment processes were more efficient than 99.9%, resulting in an average microplastic discharge for each 1400 L of treated wastewater. Also, they found that tertiary treatment
processes were effective in removing microplastics and microplastics did not observe in the final tertiary effluent of the wastewater treatment plant.

![Figure 1](image_url)

**Figure 1.** Microplastics derived from personal care products (Talvitie et al, 2017)

### References


Synthesis of NiFe LDH Deposited on Reduced Graphene Oxide for Degradation of Moxifloxacin by Sono–Photocatalytic Process

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Keywords: Layered double hydroxide; Reduced graphene oxide; Sono–photocatalyst; Nanocomposite.

Abstract

Effective visible–light photocatalyst is of great importance in photocatalytic processes. Herein, NiFe layered double hydroxide deposited on reduced graphene oxide sheets has been synthesized. The synthesized catalyst was verified by using SEM, XRD and EDS analysis. The obtained catalyst can be used as a multifunctional material for its promising applications in the field of sono–photocatalysis process to degrade refractory organic pharmaceutical.

1. Introduction

Exploring hierarchical nanocomposites with multifunctional properties through combining various building blocks together into a well-designed structure has always been a hot topic [1]. Among various building blocks, reduced graphene oxide (rGO) and layered double hydroxides (LDH) with attractive properties have been intensively investigated, recently [2]. rGO can provide the high mechanical strength, while LDH can provide the good chemical reactivity. Furthermore, graphene–based supports improve the oxidation rate of the system by trapping the photo–induced electrons [3]. Moxifloxacin (MFX) is a hazardous antibiotic drug used to treat various bacterial infections. The prepared nanocomposite can indicate an enhancement in sono–photocatalytic degradation of MFX, successfully.

2. Materials and Methods

GO dispersion was mixed with an aqueous solution of Ni(NO3)2.6H2O and Fe(NO3)3.9H2O. Then, NaOH solution (2 mol/L) was added. The mixture was stirred and transferred into a Teflon lined stainless steel autoclave. The autoclave was sited in a pre–heated oven at 110 ºC for 19 h. The obtained precipitate was completely washed with deionzed water and dried in the oven.

3. Results

Figures 1 shows SEM analysis of the synthesized catalyst in which NiFe LDH are well dispersed on the rGO sheets. The XRD pattern of the synthesized catalyst is shown in Figure 2a. The LDH shows diverse reflections corresponding to bands at 20 values of 11.3°, 23.0°, 33.5°, 38.6° and 59.7°. The weak characteristic peak at 20 = 25° can be attributed to the diffraction of rGO. The presence of Ni, Fe, O, and C in the catalyst structure is confirmed well through EDS analysis (Figure 2b).
The efficiency of the diverse processes is shown in Figure 3. The enhancement in sono–photocatalytic process can be related to the light radiation in the presence of ultrasonic waves which can provide a synergistic effect by generation of highly reactive free radicals such as hydroxyl radicals (•OH).

References

Fate and Distribution of Heavy Metals During Air-oxidant Gasification Processing of Treatment Plant Sludges

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Keywords: Treatment plant sludges, Biomass, Gasification, Renewable energy, Heavy metals

Abstract

Gasification of treatment plant sludges is considered as a promising route to recover the energy from these organic materials. Most of research has focused on the efficient valorization of the sludges and syngas production by using different gasification applications. The sludges are also categorized as biomass; however, they differ from the conventional biomass because of their typical characteristics like heavy metals. The fate and distribution of the heavy metals during gasification application has recently taken into account regarding the overall environmental assessment of the energy recovery from sludges. In this study, the fate and distribution of the heavy metals during the air-oxidant gasification pilot trials of treatment plant sludges taken from different wastewater treatment plants were examined. The characterization studies were done by using raw sludge cakes, and gasification residuals (ash and vitrified material). The leaching tests were also carried out by using the gasification residuals to determine the heavy metals content of the eluate samples. The heavy metals (Ba, Cd, Cr, Ni, Pb, Zn, Cu, Mo, As, Sb, Se, Hg) were analyzed in all samples by ICP-OES and SEM-EDS. Sample preparations for heavy metals were done according to the EPA 3051 and EPA3052 methods while the elutriation procedure described in TS EN 12457-4 standard was followed for leaching tests. All analyses were done according to Standard Methods (APHA, 2005). The distribution of the heavy metals was determined in the gasification products. The experimental results were evaluated based on the behaviors of the metals under some certain conditions depending on the gasification application regarding their properties like thermally stable and lower thermal stable metals. The volatilization and the enrichments of the heavy metals in the gasification products are discussed in details in the paper interim of sustainable and economic processing of the sludges. This study was supported by TÜBİTAK-ÇAYDAG under grant #113Y166 “Investigation of Gasification Potential of Treatment Plant Sludges” Research Project.
Chemical and Thermal Characteristics of Petro-Chemical Industrial Sludge

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Keywords: Petrochemical industry, Sludge, Gasification, Renewable energy.

Abstract

Industrial sludges have different characteristics even in the same industrial sector. The strategy development for the management of industrial sludges is a great challenge in terms of sustainable and economic concern. In addition to the legislative restrictions on the traditional recycling options including land application, agricultural usage etc., the recovery of energy and valuable materials from industrial sludges become more important. Petrochemical industry produces a large amount of sludge having different pollutants. To build an appropriate management strategy for these sludges, the first important stage is the whole and correct characterization of them. In this study, the characterization of the industrial sludge taken from a petro-chemical industry complex located in Izmir, Turkey was done. In the experimental studies, pH, salinity, electrical conductivity (EC), heavy metals, dry solid content (DS), volatile solid content (VS), loss of ignition (LOI), low heating value (LHV), total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP), FTIR, XRD, proximate and ultimate analyses, SEM-EDS, TGA/DT were determined. All analyses were done according to Standard Methods (APHA, 2005). The experimental results were especially assessed to determine the pyrolysis/gasification behavior of the sludge for energy recovery purpose. The paper discusses the experimental results in details. This study was supported by TÜBİTAK-ÇAYDAG under grant #113Y166 “Investigation of Gasification Potential of Treatment Plant Sludges” Research Project.
Inhibition Effect of Different TiO₂ Nanoparticles on the Oxygen Uptake Rate (OUR) of Activated Sludge Microorganisms

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Keywords: activated sludge, inhibition, nanoparticles, oxygen uptake rate, Titanium dioxide.

Abstract

TiO₂ nanoparticles (NPs) are the most studied ones to develop self-cleaning and antibacterial nano textiles. However, the negative effects of NPs and the risk of possible release of NPs into the wastewater process and then aquatic environment are not well known yet. Oxygen uptake rate (OUR) measurements have been realized as more reliable methods compared to instant determination of the OUR response of the activated sludge systems for toxicity and inhibition studies. Activated sludge inhibition tests of NPs applied synthetic wastewater samples, were conducted in accordance with a test procedure described by ISO 8192. Activated sludge was acclimated in lab-scale Fill and Draw Reactors (F&DRs). The EC₅₀ level as defined by ISO 8192 after 30 min and 180 min of reaction time for TiO₂ NPs was calculated and corresponds to 1654 mg/L and 1670 mg/L for Ti, respectively. EC₅₀ values of 3% Ag added to TiO₂ NPs sol-gel and 2% Cu added to TiO₂ NPs sol-gel were calculated to be 147 mg/L and 166 mg/L, 620 mg/L and 386 mg/L respectively after 30 min and 180 min of exposure times.

1. Introduction

Nanotechnologies are focused on the creation or manipulation of nanometric dimension particles and materials, (from 1 to 100 nm). Face to the growing industrial use of nanomaterials, NPs are expected in aquatic and terrestrial environments (Clement et al., 2013). TiO₂ is among the most frequently reported engineered materials used in nanotechnology-based consumer products that have been used for decades (Kiser et al., 2009). Nanotechnology is one of the most promising interdisciplinary technologies that have been spreading different sectors and becomes very indispensable for human life. In addition to these applications, in the recent years, it has been very common in environmental projects (Qian and Hinestroza 2004). Nanotechnologies/Nano-devices which remove water, air and soil pollution as an alternative treatment method, and products which cause less waste and pollution and need fewer raw materials during manufacturing are main applications of nanotechnology in environmental sector. TiO₂ NPs are widely applied in catalysts, sunscreens, cosmetics, paints, plastics and wastewater treatment processes. The occurrence of TiO₂ NPs in the environment has recently aroused public attentions regarding their potential effects on the biota and human health (Li et al., 2017). Application of nanotechnology in the textile products is still very early in its infancy but it is already proving to be a useful tool in improving the performance of textiles. TiO₂ NPs are the most studied NPs in the cotton textile industry to develop self-cleaning and anti-bacterial cotton products (Gupta et al., 2007).

Respirometry has been used very efficiently for identifying and understanding the biochemical mechanisms involved in the activated sludge process. On-line oxygen uptake
rate (OUR) measurements have been realized as more reliable methods compared to instant
determination of the OUR response of the activated sludge systems for toxicity and
inhibition studies (Karahan, 2010). A number of successful applications of respirometry
have been reported which have been used to understand and predict different biochemical
mechanisms of activated sludge systems (Meriç et al., 2003; Karahan, 2010; Čalhan, 2012).

This study aims to investigate inhibition effects imposed by sol-gel based TiO\textsubscript{2} NPs of
activated sludge system using OUR. In this context, this study will provide a better
understanding of the inhibition mechanisms and the results of the study will be useful in the
solution of operational problems of activated sludge systems.

2. Materials and Methods

The experimental setup has been prepared with the acclimation of activated sludge obtained
from a domestic wastewater treatment plant with a synthetic sewage described by ISO 8192
(ISO 8192, 2007), in a Fill and Draw Reactors (F&DRs). The standard solutions of NPs
with an initial concentration 1 or 2 g/L of the tested NPs soles and NPs soles with metals
(3% Ag and 2% Cu) were freshly prepared by dissolving in bidistilled water. All chemicals
used were of analytical grade. Furthermore, the pH value of all F&DRs were adjusted to 7 ± 0.2,
prior to the inhibition tests, by the addition of 1 N HCl or 1 N NaOH solutions.

2.1 Activated sludge inhibition tests

OUR measurements have been realized as more reliable methods compared to instant
determination of the OUR response of the activated sludge systems for toxicity and
inhibition studies. The aim of this study is to investigate inhibition effects imposed by sol-
gel based TiO\textsubscript{2} NPs of activated sludge system using OUR. Activated sludge inhibition tests
of NPs applied synthetic wastewater samples, were conducted in accordance with a test
procedure described by ISO 8192 (ISO 8192, 2007). The experimental setup has been
prepared with the acclimation of activated sludge taken from a municipal wastewater
treatment plant in Denizli, Turkey. Activated sludge was acclimated in two lab-scale
F&DRs, which had a working volume of 2 L. The reactors had hydraulic retention time of
1 day and it was fed with synthetic sewage representing domestic wastewater at fixed F/M
ratio of 0.3 mg COD per mg VSS per day. 16 g peptone, 11 g meat extract, 3 g urea, 0.7 g
NaCl, 0.4 g CaCl\textsubscript{2}.2H\textsubscript{2}O, 0.2 g MgSO\textsubscript{4}.7H\textsubscript{2}O, and 2.8 g K\textsubscript{2}HPO\textsubscript{4} were dissolved in 1 L of
distilled water to prepare synthetic sewage stock solution. Hach nitrification inhibitor,
Formula 2533\textsuperscript{TM} was added to the reactors at a concentration of 0.16 g for 300 mL volume.
The reactors were aerated so that the dissolved oxygen levels were above 5 mg/L, pH was
checked periodically and it was always between 6.5 to 7.5 during the experiments.
Dissolved oxygen measurements were performed by a WTW Inolab OXI 740 model oxygen
meter in 50 mL air-tight vessels. Repeated experiments were performed by using TiO\textsubscript{2} NPs,
prepared with sol-gel method, for periods of 30 to 180 min.

3. Results

The respirometric assessment of the inhibitory impact of TiO\textsubscript{2} NPs and TiO\textsubscript{2} NPs with metal
doped which has the best self-cleaning and anti-bacterial properties on substrate utilization
by activated sludge has been performed with the synthetic sewage (peptone-meat extract)
as described with the standard procedure (ISO 8192, 2007). The ISO procedure requires
running a set of aerated batch reactors with a range of inhibitor concentrations, using the
synthetic sewage and biomass previously acclimated to the substrate adjusted to fixed an
initial food to microorganism (F/M) ratio of 0.3 mg COD per mg VSS per day. The EC\textsubscript{50}
level as defined by ISO 8192 after 30 min and 180 min of reaction time for TiO\textsubscript{2} NPs was
calculated and corresponds to 1654 mg/L and 1670 mg/L for Ti, respectively.
In the activated sludge system on the microorganisms more evident inhibition effect was observed when TiO2 NPs were doped with copper (2% Cu added to TiO2 NPs sol-gel) as EC50 values were calculated as to be 620 mg/L and 386 mg/L after 30 and 180 min of exposure times respectively. However, Silver has more inhibition effect on the microorganisms than copper added solution in lower concentrations. As a result of 30 and 180 minutes reaction time of 3% Ag added NPs EC50 values were obtained as 147 mg/L and 166 mg/L, respectively. The experimental data on all figures indicate that a good logarithmic correlation between the inhibitor concentration and percent decrease in the corresponding OUR level for the range of TiO2 NPs concentrations tested in the study.

4. Conclusion

In this study, it is investigated that the toxicity effect on the microorganism in the activated sludge, of the NPs which are emerged by being used in nano technological coatings, to give the features to the fabric in the textile industry. TiO2 NPs and two metal doped TiO2 NPs were selected and applied, in this study. By monitoring the OUR of the activated sludge the effects of biological treatment system is investigated. The titanium (Ti) concentration was found as EC50 inhibition concentration at the point of 50% of OUR was blocked.

The EC50 level after 30 min and 180 min of reaction time for TiO2 NPs was calculated and corresponds to 1654 mg/L and 1670 mg/L for Ti. TiO2 NPs with metal doped which has the best anti-bacterial and self-cleaning properties after 30 min and 180 min of reaction time, EC50 values of 147 mg/L and 166 mg/L, 620 mg/L and 386 mg/L were obtained as a result. Silver which is known to have anti-bacterial properties has more inhibition effect on the microorganisms than copper added solution in lower concentrations.

It is thought to get more realistic results in the case of the study is carried out with the textile wastewater in the biological treatment system, TiO2 particles mixed with activated sludge and treated water have been found that only very small concentrations because of the adsorption and precipitated on activated sludge. It is expected that this study can contribute to ongoing and future studies to understand the TiO2 NPs inhibition effect on the activated sludge system.

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References

Recycling Possibility of the Antioxidants in Olive Mill Wastewater by an Integrated Process

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Keywords: Olive mill wastewater treatment, recycling, phenolic antioxidant, hydroxytyrosol, mechanical vapor recompression evaporator

Abstract

A number of phenolic compounds (PCs) and their environmental contamination problems as consequences of olive oil production process in the countries surrounding the Mediterranean Sea propel the need for recycling of olive mill wastewater (OMWW) as potential source of high-added value phenolic antioxidants to reduce the toxicity of the effluent. Since existing treatment methods are not efficient for extracting the antioxidants from OMWW due to the consumption of high amount of solvent, new treatment methods will still be on-demand in foreseeable future. This research utilizes concentrated decanter and lagoon OMWW treated with mechanical vapor recompression evaporator (MVRE) as source of natural antioxidants mainly hydroxytyrosol (HTyr). A multistage recycling process including acidification, delipidization, solid-liquid extraction (SLE) with two different solvents and two different systems and solid phase extraction (SPE) using nonionic polymeric adsorbent was applied to both types of concentrates. While more than 90 % protein and carbohydrate elimination from the concentrates were achieved with SLE using 80 % ethyl acetate in water, highest HTyr recovery (6.6 mg/g) was achieved with ethanol-salt in aqueous two-phase extraction (ATPE) system and further SPE was required to purify the ethanol extract of ATPE. The results showed that the selectivity of XAD16N for HTyr was pretty high with 81 % recovery from ethanol extracts of both concentrates.

1. Introduction

High pollution load of wastewater occurred from olive oil production process and associated environmental concerns are some of the most important problems of the worldwide olive oil industry. Turkey like other Mediterranean countries is facing severe environmental pollution problems due to toxic characteristic and high chemical oxygen demand (COD) of OMWW. With the introduction of continuous processes in the production of olive oils, the volume of produced wastewater has increased, and the problem became even worse in this agricultural sector. PCs are highly responsible for low biodegradability and toxicity of OMWW and most of these PCs have antioxidant properties. Since current chemical and enzymatic processes for the synthesis of phenolic antioxidants such as HTyr are very slow and expensive, the recovery of these compounds from a natural waste source, OMWW, creates an environmentally safe and sustainable recycling process of OMWW as well as a promising field for the market introduction and establishment of phenolic antioxidants.
2. Materials and Methods

Two different types of OMWW concentrate (OMWC) were selected in this research as sources of phenolic antioxidants to compare their physicochemical characteristics, antioxidant capacity, and antioxidant recovery efficiency. A multistage recycling process of OMWW was initiated by reducing the water content of OMWW in a pilot scale MVRE operated in Ayvalık district of Balıkesir. Then, the concentrated wastewaters were pretreated prior to extraction stages by the employment of oil removal and acidification. The partitioning of target antioxidant in organic phase during SLE was performed by using ethyl acetate and ethanol. SLE conditions were optimized by considering the effects of solvent to sample ratio, extraction time, extraction stage, and the temperature. ATPE with ethanol was accomplished by using salting out. The extracts of ethanol were further purified by polymeric adsorbent XAD16N. Total phenolic content of samples was determined colorimetrically according to Folin-Ciocalteu method. The quantification of HTyr was performed by LC-MS/MS analysis. The antioxidant activity of extracts was estimated by 2,2-diphenyl-1-picrylhydrazyl radical scavenging assay. The further characterization of samples was carried out by their moisture, organic carbon, TKN, pH, lipid, carbohydrate, and protein contents.

3. Results

As shown in Figure 1 both lagoon and decanter OMWCs were subjected a multistage process for the recovery of HTyr, which is the most abundant antioxidant in OMWW. The physical and chemical characteristics of OMWCs exhibited considerable variations. The OMWC of lagoon sample, which was very viscous and sticky, has about two-fold higher protein content than that of decanter sample. While the lipid content of decanter OMWC was 88 mg/g, it was lower than 1 mg/g for the lagoon OMWC.

![Figure 1. A multistage recovery process for HTyr from OMWW.](image-url)
Hexane extraction which was only applied to decanter sample and pre-acidification enhanced the extractable phenolic antioxidants and also reduced other organic constituents of the samples. In SLE stage of the process, ethanol provided relatively poor elimination rates for proteins and carbohydrates from the extracts of both samples compared to ethyl acetate. However, the application of SPE to ethanol extracts of ATPE provided both further purification of samples and the concentration of HTyr. Consequently, 6.6 mg/g of HTyr was achieved from decanter sample by ATPE at 65°C within 60 min extraction period.
Towards Sustainable Agricultural Waste Management: Reuse and Energy Recovery Potentials for Turkey

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Keywords: Agro-wastes, anaerobic digestion, biogas, energy crop, sustainability, wastewater sludge.

Abstract

A growing concern has emerged during the recent years for innovative and economically viable opportunities for sustainable agriculture. Modern agriculture is heavily dependent on non-renewable energy sources, especially petroleum. The continued use of these energy sources are not economically feasible and cannot be sustained indefinitely. In sustainable agricultural systems, there is a reduced reliance on non-renewable energy sources and a substitution of renewable sources by using agro-wastes (crops residuals, etc.).

Agricultural waste is mainly produced as a result of various agricultural operations. The crops and livestock account for 90 percent of the agricultural sector in Turkey. Recently, the researches on agricultural waste has focused on the organic materials, particularly the crops residuals resulting from crop cultivation activities, as a promising source of energy supply for production and processing. These residues are generally treated in an uncontrolled manner, burned in open-air fires or allowed to decay. In either case, they result in significant environmental impacts while at the same time potentially useful resources are wasted.

The biological stabilization of agricultural wastes have many advantages like improved efficiencies in anaerobic biodegradability and in higher biogas yields. Biogas is a widely applied technology in the World that use wet heterogeneous ‘waste’ biomass and produce energy, retain a proportion of the organic matter and potentially recycle farm nutrient. The production of biogas to reduce the CO₂ emissions is also one of the key strategic approaches in Turkey.

The aim of this research is to investigate the existing agricultural waste management approaches, exploit the potential of agricultural waste residues in Turkey and study the biogas production potential through the anaerobic batch biodegradation of selected agricultural product residuals such as corn silage, olive pomaces, etc. co-digested with the wastewater treatment plant sludges. For the biogas production studies, the characteristics of selected types of materials and wastewater sludges were analyzed and anaerobically digested in borosilicate glass reactors at mesophilic conditions.

In order to understand and compare the degree of waste stabilization throughout the study, gas samples collected from the reactors were monitored regularly. The amount of biogas production in the reactors was measured by the Miligascounters (Ritter MGC-1). The gas composition (CH₄ and CO₂) analyses were realized by using a Gas Chromatograph (GC HP 5890).
The mixtures of substrates and sludge was analyzed for Total solids (TS), volatile solids (VS), suspended solids (SS), chemical oxygen demand (COD), volatile fatty acids (VFA); pH, alkalinity; oxidation-reduction potential (ORP), total Kjeldahl Nitrogen (TKN), ammonia nitrogen (NH₄), total phosphate (PO₄) and total organic carbon (TOC). All these analyses were performed according to the Standard Methods for the Examination of Water and Wastewaters (APHA, AWWA- WPCF, 2006).

The results of the study revealed that the existing agro-waste/biomass potential in Turkey should be focused urgently towards clean and sustainable energy sources. The laboratory studies showed that the co-digestion of wastewater sludge with the agricultural residues appeared to be more effective in terms of biogas production than the single-substrate digestion.
Comparative Evaluation of Biogas Recovery During Anaerobic Treatment of Aircraft Deicing Fluids at Increased Ratios in Domestic Wastewater

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Keywords: Aircraft deicing fluids; anaerobic reactor; energy recovery; methane production; propylene glycol

Abstract

Anaerobic treatability of domestic wastewater contaminated with two different types of aircraft deicing fluids (ADFs) at different ratios (i.e., Type 1: 0-9.7% and Type 2: 0-12.5%) was comparatively investigated using batch reactors operated at mesophilic condition (35°C). In this respect, ADF ratios yielding inhibitory effect on anaerobic cultures were determined according to the biogas yields at the end of incubation. Results indicated that excluding the control reactors; the highest biogas yields were calculated as ∼0.23 and 0.27 m³/kg tCOD fed in the bioreactors having 1.1% and 1.8% Type 1 and Type 2 ADFs, respectively. In the reactors with ≥5% Type 1 and ≥2.0% Type 2 ADFs indicated inhibition on anaerobic treatability with significant reductions in the biogas yields. Hence, it is considered that ADF-contaminated wastewaters should be at appropriate ratios before they are treated by anaerobic systems in full-scale reactors at the airports.

1. Introduction

According to the air transportation statistics of Turkey, annual total domestic and international traffic was more than 1,500,000 in the past two years. Respectively, the amount of pollutants at the airports increase especially due to the spent de-icing/anti-icing fluids which are generally used in order to provide flight safety. Because, any snow or ice on a critical surface of an aircraft must be removed before departure during flight operations at frosted conditions. Aircraft deicing fluids (ADFs) are sprayed under pressure immediately after diluted with hot water (55-80°C). ADF is composed of mainly glycol (i.e., ethylene or propylene) and there are four ADF types commonly used with different glycol/additive contents (e.g., Type I fluid with short holdover time is about 90% glycol, 8% water, and <2% additives, but it is diluted as needed depending on ambient temperatures). Although the primary environmental concern with deicing/anti-icing operations has been attributed to the glycols; their excessive usage, high organic strength [i.e., total COD (tCOD) of the ADF-contaminated wastewaters could reach to ca. 90,000 mg/L] and biodegradability threatens oxygen depletion in surface waters due to uncontrolled runoff. ADFs are discharged through the grids/channels found in special parking areas at airports (de-icing pads) and the spent ADF is commonly stored in a storage tank. ADFs might also reach to the nearest municipal Wastewater Treatment Plant (WWTP) at certain ratios through sewerage system due to snow melting. Additionally, attention has shifted to the potential toxic effects from additives, specifically corrosion inhibitors because ADFs are propylene glycol-based fluids containing water, corrosion inhibitors, wetting agents, and dye. Hence, it is very important...
to treat/manage these wastewaters by sustainable methods. One of the most suitable options for treating ADF-contaminated wastewaters and glycol-based high strength wastes is anaerobic treatment. Propylene glycol undergoes an initial disproportionation reaction into n-propanol and propionate which are oxidized to propionate and to acetate (both releasing hydrogen), respectively while aceticlastic and hydrogen-oxidizing methanogenesis continues. By anaerobic treatment, it is also possible to recover biogas, which is a renewable energy source making this method more sustainable compared to other energy-consuming treatment technologies. Previous studies on anaerobic treatment of high glycol containing wastewaters reported ∼0.3 m³/kg COD biogas yield with 77% methane content. However, ADFs negatively affect the performances of the biological treatment processes above a certain ratio and they might inhibit anaerobic cultures leading to low biogas productions especially during anaerobic treatment. Hence, their contributions to the influent of municipal WWTPs should be pre-determined. The objectives of this study are to comparatively investigate anaerobic treatability of domestic wastewater contaminated with Type 1 and Type 2 ADFs at increased ratios and to determine their threshold ratios in domestic wastewater in order not to cause any inhibition on biogas recovery.

2. Materials and Methods

ADFs and domestic wastewater are provided from one of the airports in Istanbul. Anaerobic treatment was conducted in N₂-flushed, 1 L glass flasks. Control reactors were run with the addition of only domestic wastewater and seed sludge. The inoculum was the granular sludge from a mesophilic anaerobic digester treating pulp/cardboard industry. Bioreactors were operated by the introduction of ADFs with the following ratios: Type 1: 0, 1.1, 3.4, 5.2, 9.7% and Type 2: 0, 1.8, 2.7, 4.8, 8.3, 12.5%. Reactors were run in the batch-mode at 35°C constant temperature room (i.e., mesophilic) until the changes in cumulative biogas production volumes were negligible and stopped. Conventional parameters were measured according to Standard Methods; VFAs were measured by Agilent Technologies 6890N gas chromatography; and propylene glycol was determined by Bellingham+Stanley Abbe (60/70 model) refractometer. Gas productions were daily monitored by Lutron PM-9107 manometer from the headspaces and biogas composition was determined by ABB-brand, The Advance Optima process gas analyzers equipped with thermo-magnetic and infrared photometers.

3. Results and Discussion

At the end of anaerobic treatment, respective tCOD removals were about 86% and 63% (Figure 1 a-b) yielding maximum biogas yields of ca. 0.22 and 0.25 m³/kg tCOD fed and methane contents of ca. 63% and 60% for Type 1 (1.1%) and Type 2 (1.8%) ADFs. Findings of this study also indicated that these ADFs might have inhibitory effect on methanogenic cultures showing significant reductions in biogas yields above certain ratios (Figure 1c). The change in VFAs and pH values also indicated compatible results that VFAs accumulation occurred when substantial pH decreases were observed beyond certain ADF ratios.
Figure 1. COD changes and removals for Type 1- (a) and Type 2– (b) contaminated wastewater and biogas yields (c).

Acknowledgement

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Comparative Efficiency and Environmental Impact Assessments of a Solar-Assisted Combined Cycle with Various Fuels Options

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Keywords: Biomass, CO\textsubscript{2} emission, Efficiency, Gasification, Thermodynamic analysis

Abstract

Due to resources depletion and non-sustainable resources, fossil fuels are not capable of compensating the growing energy needs. In addition, the easily extractable fossil fuels are facing an increase in their prices. It is worth mentioning that the greenhouse gases (mainly CO\textsubscript{2}) have been accumulated in the atmosphere caused by essentially burning fossil fuels. Therefore, clean and sustainable energy options have become much more important and researches have been intensified to make it more affordable and productive. In the present study, a solar-assisted combined cycle is developed and investigated for the three different types of fuel (wet wood, sawdust and coal) so as to compare the CO\textsubscript{2} emissions and evaluate the system in terms of effectiveness. The highest CO\textsubscript{2} emission rate is determined for the coal with 21.85 kg/s, and the lowest CO\textsubscript{2} emission rate is observed for the sawdust with 13.29 kg/s. Moreover, a comprehensive thermodynamic analysis, including all stream points, is carried out for the designed system by using Engineering Equation Solver software. The highest overall energy and exergy efficiencies are calculated to be 22.8\% and 20.2\% for the wet wood, while the equivalence ratio is equal to 0.45.

1. Introduction

It is generally held that the present production and use of energy pose a serious threat to the global environment, particularly in relation to the emission of greenhouse gases (principally, carbon dioxide, CO\textsubscript{2}) and the perceived influence of these gases on the Earth’s climate. Accordingly, industrialized countries are examining a whole range of new policies and technology issues to make their energy futures ‘sustainable’ [1].

To reduce the use of fossil fuels and increase self-sufficiency in energy, nowadays, there is an increasing interest to produce heat, power and transportation fuels from renewable resources. Solid biomass is one of the most important renewable energy sources for meeting this target [2]. Since biomass is renewable and consumes atmospheric CO\textsubscript{2} during growth, it can have a small net CO\textsubscript{2} impact compared to fossil fuels. Initially, solid biomass should be converted into the syngas through the gasifier unit. Biomass gasification is recognized as a complicated process, which is affected by various parameters, including gasification medium, biomass composition, moisture content, gasification temperature and pressure, and process configuration [3].

In the present study, the main objective is to develop and investigate a solar-assisted combined cycle operated for three different types of fuel, namely, wet wood, sawdust and coal in order to compare the CO\textsubscript{2} emissions and overall energy and exergy efficiencies. In addition, a follow-up study is performed on the gasification and combustion processes for each fuel and the effects of the equivalence ratio on the overall system performance are then
investigated. Furthermore, entropy generations, exergy destructions and energy and exergy efficiencies are determined for each component of the system, comprehensively to give a practical and detailed spectrum of the whole system.

2. System Description

The proposed combined cycle is shown in Figure 1. The system comprises three main subsystems including the solar-driven system, Rankine cycle and Brayton cycle. The system is designed to operate by utilizing either biomass or coal as fuel. In other words, while valve 1 is opened, valve 2 is shut-downed.

According to the principle of the Brayton cycle, air is compressed in the turbine compressor. The air is then mixed with fuel, and burned in the combustor. In order to obtain higher efficiencies, both biomass and coal enter the gasifier units priorly the combustion process and convert into the syngas by reacting with the supplied air. The product gases of the combustion process expand in the gas turbine blades to perform mechanical work. On the other hand, the solar-driven system including numerous huge parabolic trough collectors are supposed to transfer the solar energy to the heat transfer fluid. Due to the working temperature range Therminol 66 is chosen as heat transfer fluid.

In the present study, thermodynamic analysis of the designed system is conducted for the three different types of fuel (wet wood, sawdust and coal) so as to compare the CO₂ emissions and evaluate the system in terms of effectiveness. The ultimate and proximate analysis of the wet wood (CH₁.₄₆O₀.₆₄N₀.₀₀₂), are tabulated in Table 1.

<table>
<thead>
<tr>
<th>Ultimate analysis</th>
<th>Proximate analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Element</td>
<td>Mass Percent</td>
</tr>
<tr>
<td>C</td>
<td>50.41</td>
</tr>
<tr>
<td>H</td>
<td>6.15</td>
</tr>
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</table>

Table 1. Ultimate and proximate analysis of the wet wood [4].
The chemical equation of the gasification process by neglecting the small amount of nitrogen contained in biomass can be written as follows:

\[ \hat{n}CH_{1.46}O_{0.64} + \hat{n}xO_2 + \hat{ny}N_2 \rightarrow \hat{n}CO + \hat{n}aH_2O + \hat{n}bH_2 + \hat{ny}N_2 \]  

(1)

Here, \( \hat{n} \) denotes the molar flow rate of the biomass and \( x, y, a, \) and \( b \) are the coefficients of the oxygen, nitrogen, steam and hydrogen, respectively. These coefficients vary depending on the equivalence ratio.

\[ x = 1.045ER, \quad y = 3.95ER, \quad a = 2x - 0.36, \quad \text{and} \quad b = 1.09 - 2x. \]

By considering all useful outputs and total inputs, overall system energy and exergy efficiencies can be written as follows [5]:

\[ \eta_{overall} = \frac{W_{net}}{m_{fuel} \times LHV_{fuel} + \dot{E}_{Solar}} \]  

(2)

\[ \psi_{overall} = \frac{\dot{W}_{net}}{m_{fuel} \times (ex_{ph} + ex_{ch})_{fuel} + \dot{E}_{X_{Solar}}} \]  

(3)

3. Results and Discussion

A comprehensive thermodynamic analysis, including all stream points, is carried out for the designed system by using the Engineering Equation Solver software which can evaluate the thermodynamic state properties of different substances through built-in internal functions. Additionally, both energy and exergy evaluations are conducted in various operating conditions and design parameters such as equivalence ratio. Moreover, the entropy generations and exergy destructions are determined for each component in the system.

In order to compare the CO₂ emissions of the different types of fuel, chemical equations of the gasification and combustion processes are composed for the each fuel. The highest CO₂ emission rate is determined for the coal with 21.85 kg/s, and the lowest CO₂ emission rate is observed for the sawdust with 13.29 kg/s as shown in Figure 2. On the other hand, while proposed system operates by using coal as fuel, 36.19 MW net work output is obtained. The highest amount of air is required during the coal gasification process with 22.35 kg/s.
In Figure 3, it is illustrated that how overall energy and exergy efficiencies of the designed system change, depending on the equivalence ratio for each fuel. The highest overall energy and exergy efficiencies are determined for the wet wood with 22.8% and 20.2%, respectively while equivalence ratio is equal to 0.45.

Conclusions
In this paper, a solar-assisted combined cycle is developed and thermodynamically analysed for three different types of fuel through energy and exergy approaches. The key findings may be stated as follows:

- The highest CO₂ emission rate is determined for the coal with 21.85 kg/s, and the lowest CO₂ emission rate is observed for the sawdust with 13.29 kg/s.
While the proposed system operates by using coal as fuel, a total net work output of 36.19 MW is obtained. The highest amount of air is required during the coal gasification process with 22.35 kg/s.

The highest overall energy and exergy efficiencies are determined for the wet wood with 22.8% and 20.2%, respectively while the equivalence ratio is equal to 0.45.

References

Water Clarification: Molecular Dynamics Simulation of Kaolinite-Water Interface in Saltwater for a Range of pH Values

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Keywords: Kaolinite, saltwater, kaolinite-water interface, cation adsorption, water orientation

Abstract

Kaolinite is the most abundant type of autigenic clay in mineral and rock deposits; it is a stratified hydrated silicate mineral, Al₂O₃.2SiO₂.2H₂O, with a tetrahedral silica sheet bonded through oxygen atoms to an octahedral sheet of alumina. The electrical charge density and the coexistence of anionic and cationic sites on the basal planes and edges promoting various associations between kaolinite particles reveal the difficulty in separating particles from water. This is a great concern in mineral-rich regions facing serious water shortages. The mining industry makes every effort to close the water cycle, however, the water lost to tailings often exceeds 0.75 m³/ton of ore processed. In the short term, mining expansion plans do not seem feasible unless seawater is used raw or partially desalinated, however, the electrolytes pose an additional difficulty by altering the surfaces of both mineral particles and flocculant affecting the water clarification operation. Thus, it is of great interest to reveal the behavior of the kaolinite-water interface in the presence of electrolytes for a range of pH values.

1. Introduction

 Schofield and Samson (1954) have shown that the edge face of kaolinite crystals should, at acid pH, adsorb one Cl⁻ for each 33 Å². Further, these authors noted that for alkaline conditions of about pH 6.5 in 0.005 M NaCl the clay exhibited a negative adsorption. However, Quirk (1960) reported a positive adsorption dependent on concentration under conditions as alkaline as pH 10. When allowance is made for this positive adsorption the correct value is obtained for the surface area. Later, Wahlberg and Fishman (1962) found the smallest values for the distribution coefficient of adsorbed Cs on kaolinite as compare to several other clays. The distribution coefficient at a Cs concentration of 0.01 N was low and about the same for each of several competing cations. Molecular dynamics simulations have been particularly suitable to clarify ion adsorption on kaolinite surfaces. Vasconcelos et al. (2007) used molecular dynamics to study the mechanisms involved in the adsorption of various ions to the basal surfaces of kaolinite. According to these authors, cations and anions adsorb preferably on the siloxane and gibbsite surfaces of kaolinite, respectively. Cs⁺ form strong inner-sphere complexes at ditrigonal cavities on the siloxane surface. Outer-sphere cesium is highly mobile and only weak adsorption may occur. A small amount of Na⁺ adsorbs on the siloxane surface as inner-sphere complexes at less clearly defined sites. Like Cs, Na only forms very weak outer-sphere complexes on this surface. Li et al. (2015a) by means of molecular dynamics simulations found that defect sites on clay particles
promote the adsorption of metal ions; in addition, these authors found that the adsorption capacities are closely associated with ionic concentrations, defect sizes and contents. The work of Li et al. somehow reconciled contradictory experimental observations of adsorption on kaolinite.

2. Materials and Methods

Here, we use \textit{ab initio} calculations to obtain charge densities on crystalline kaolinite edges and the corresponding charge delocalization after varying degrees of deprotonation of silanol and aluminol groups (Quezada et al. 2017). Then, we use classical molecular dynamics to study the interaction of water with the charged kaolinite edges in the presence of aqueous solutions of the complete series of monovalent alkali and alkaline-earth metal chlorides. Salt concentration was high and equal to 0.66 M, equivalent to the ionic strength of seawater. The Gromacs 5.0.2 molecular dynamics simulation package (Berendsen 1995) was used with the SIMD instructions AVX_256 and GPU enablement to accelerate the calculations. The Berendsen modified thermostat and Berendsen barostat were used (Berensen et al. 1984, Bussi et al. 2007). The particle mesh Ewald method (PME) was used (Darden et al. 1993) to compute long range interactions. We used the CLAYFF force field33 modified to incorporate deprotonation of silanol and aluminol surface groups. The SPC/E water model was used to describe water. For the ions, Lennard-Jones 12-6 parameters derived from Li and Merz (2014) and Li et al. (2015) were used adjusted to the SPC/E water model (Berensen et al. 1987).

3. Results

Results here include cation density profiles, total number of cations adsorbed, sequentially adsorbed layers of monovalent and divalent cations and adsorption patterns, effect of cations on the orientation of water molecules close to the surfaces, and the distance at which the surface becomes neutral or reverses its charge (see Figure 1). The results of this work are expected to contribute new knowledge on the interaction of mineral oxides with macromolecules in saltwater, for example, polyelectrolytes in solid-liquid separation processes.

Figure 1. Cation adsorption (a); density profile (b); adsorption layers (c) inner shell A, (d) second shell B, (e) diffuse shell C; water orientation at kaolinite-water interface (f).

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Micropollutant Removal from a Secondary Treated Municipal Wastewater by Electrodialysis

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Keywords: Micropollutants, Electrodialysis, Municipal wastewater, Membrane technology.

Abstract

Wastewater has become a general problem in the C21st with tons of domestic wastewater being released back to the environment without prior treatment—this has led to adverse impacts on the aquatic ecosystem due to the presence of numerous micro-pollutants. To investigate micro-pollutant occurrence and subsequent removal rate in a secondary treated municipal wastewater electro-dialysis was chosen as a method for advanced treatment. The applied direct current drives the electro-dialysis process whereby ion separation occurs and cations and anions migrate towards cathodes and anodes, respectively; making it easier to remove certain species in wastewater. The study utilizes this property to investigate the efficacy of ED to remove micro-pollutants across the ion-exchange membrane. The removal of a number of micropollutants was investigated under a continuous electrodialysis experiments. Apart from Ibuprofen and sulfamethoxazole almost all the target micropollutants under study has obtained retention/removal rate higher than 85%. Limited leakages and subsequent infiltrations occurred after longer operating times to limit substantial breakthrough and membrane fouling the study used ion exchange column as a preliminary treatment to reduce hardness. In general the study shows the applicability of ED in wastewater treatment can offer a better alternative.

1. Introduction

Micropollutants are organic substances that are present in water. They include many synthetic substances as well as natural substances such as pharmaceuticals, personal care products, steroid hormones, pesticides and many other emerging substances. These substances are found in low concentrations (nanograms or micrograms per liter) and are diverse which in turn complicates their detection and create challenges in municipal wastewater treatment plants (MWTP) facilitating their release into the environment. Their occurrence has been associated with a number of negative effects for example micropollutants can be harmful to fragile aquatic life i.e they influence the growth, and effect the reproduction of fish and amphibians, cause damages to the nervous systems of aquatic organisms, faze or inhibits algal photosynthesis and in general effect biochemical process in nature.

Tons of municipal wastewater are being released from municipal wastewater treatment plants (MWTP) thus making MWTP’s a significant and continuous source of input of these micropollutants. In addition to this current existing MWTP are unable to detect and remove these substances therefore many of them are able to pass through the wastewater treatment processes due to the fact that they are non-biodegradable and do not adsorb readily.

Despite the fact that they are found in low concentrations, their continues introduction into the aquatic environment exposes aquatic organisms to be permanently under this pollution. Hence measures are necessary at various levels to achieve a significant reduction in the
discharge of micropollutants from municipal wastewater. Particularly advanced wastewater treatment is required for this goal to be realized thus, in this study electrodialysis was selected and employed as an advance treatment method in a secondary treated domestic wastewater.

2. Materials and methods

2.1. Electrodialysis equipments

Experiments were carried out with a PCCell ED 64-002 stack manufactured by PCCell GmbH, Heusweiler, Germany. Four bolts at each corner side of the stack are used to hold membranes and spacers together. The bolts are equally tightened by using a torque wrench applying a torque of 6 Nm. The stack configuration is composed of 2 cation exchange membrane 1 anion exchange membrane separated by 4 spacers with a thickness of 0.5 mm. All membranes and spacers are supplied by PCA (PolymerChemie Altmeier GmbH, Heusweiler, Germany).

3. Experimental procedures

To reduce membrane fouling, ion exchange was applied as a preliminary treatment to decrease hardness that might lead to membrane fouling and a decreased level of performance. Then subsequently fed to the ED after the experiments were done. Samples from both concentrate and dilute chambers were collected and tested to monitor the systemic retention and removal of micro-pollutants during continues experiment of a secondary treated municipal wastewater using ultra-performance liquid chromatography (UPLC). Target micro-pollutants were examined in 38 wastewater samples (18 from dilute, 18 from concentrate, and 2 as control samples).

4. Results

After ED treatment target micropollutants were tested the following removal/retention results were obtained for each: Bisphenol A (97.4%), Estriol (96.6%), Estrone (92.9%), Diclofenac (92.0), Carbamazepine (80.8%), and for Estrodiol 94.3%. Only Ibuprofen and sulfamethoxazole obtained lower retention ratios (72.1% 74.5% respectively) due to some permeation in membranes. Apart from Ibuprofen and sulfamethoxazole, the study managed to obtain a removal/retention percent higher than (85.5%) for target micro-pollutants and in-turn reduces it to allowable discharge limits. Thus, applicability of ED in wastewater treatment can offer a better alternative. The overall performance of micropollutants are shown in the following figures.
The study has also been targeting the capability of the system to produce hydrogen from the wastewater and its subsequent collection at the cathode chamber. The following reaction occurs at the cathode and the anode in the case of electrolysis.

**At the cathode**

\[ 4H^+ + 4e^- \rightarrow 2H_2 \]

Eq 1

**At the Anode**

\[ 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \]

Eq 2

As illustrated in the above equation, hydrogen productions were expected to occur at the cathode thus the ED system was modified to collect the hydrogen gas being produced in that chamber.
The obtained results are still under evaluation however the recovery and collection of hydrogen gas from ED has been successful.
Decreasing Toxicity and Increasing Biodegradability of Dye Production Industrial Wastewater by Pre-Ozonation and Fenton Oxidation; Cost-Benefit Analysis of Wastewater Reuse System in Circular Economy Perspective

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Abstract

Dyes are soluble at some stage of the application process and they are used to impart color to materials. A colored dye has been accomplished in the synthesis of dye using a chromogen-chromophore with auxochrome. The aromatic structure chromogen contains benzene, naphthalene, or anthracene rings. Color giver chromophore group is represented by the following radicals, which form a basis for the chemical classification of dyes when coupled with the chromogen: azo (–N=N–); carbon (=C=C=); carbonyl (=C=O); carbon-nitrogen (>C=NH or –CH=N–); sulfur (>C=S) and other nitrogen-carbon-sulfur groups. The chromogen-chromophore structure is often not sufficient to impart solubility and cause adherence of dye to fiber by bonding affinity group. The bonding affinity or auxochrome groups are amine, hydroxyl, carboxyl, and sulfonic radicals, or their derivatives. Dyes are synthesized in a reactor, filtered and blended with many other additives to produce the final product. The synthesis step involves reactions such as sulfonation, halogenation, amination, diazotization, and finally separation processes that may include precipitation, filtration and crystallization. Dye production industrial wastewater resulting from dye filtration and equipment cleaning after batch operation can contain organic residues. As a result, dye production industrial wastewater contain toxic and non biodegradable many different compound mixture. Dye production industrial wastewater treatment system normally includes neutralization, flocculation, coagulation, settling, carbon adsorption, detoxification of organics by oxidation (using ultraviolet systems or peroxide solutions), and biological treatment. Thus investment and operational cost of dye-production wastewater system is very high and the industry needs some cost effective new approaches.

In this study, pre ozonation and Fenton oxidation were applied to increase biodegradability of highly toxic real dye production wastewater. Treatment performances of Fenton and ozonation experiments were evaluated by monitoring acute toxicity (Microtox), biological oxygen demand (BOD), chemical oxygen demand (COD), color and BOD/COD ratio. The circular economy offers a new way of looking at the relationships between markets and resources, promoting sustainable and resource-efficient practices. In this study, cost-benefit analysis of alternative wastewater reuse systems including acid recovery, pre-oxidation, biological treatment and membrane systems were evaluated in circular economy perspective.
Acknowledgement

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Decolorization and Detoxification of Textile Wastewater by Innovative and Cost Effective Ion-Exchange Process

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Keywords: Color removal, hydrothermal regeneration, ion exchange, reactive dye, textile wastewater

Abstract

Global water use is increasing due to population and economic activities growth. To tackle these challenges and build a more sustainable living condition, a shift from conventional wastewater treatment systems to source recovery oriented and eco-friendly technologies is taking a place. Textile processes are water intensive industry, and many different toxic dyes, chemicals and additives are used in the wet textile processes. Reactive azo dyes, the most used synthetic dyes in synthetic-cotton textile industries, are known to have carcinogenic and mutagenic effects. Advanced oxidation and membrane separation processes are widely used for removal of organic and inorganic pollutants. However investment and operational costs of both processes are high. In contrast, due to its low investment and operational costs, ion exchange (IE) process is widely used for many different water and wastewater applications. The removal of color with ion exchangers has been a challenge for many years. However, regeneration of the ion exchangers with conventional anionic or basic solutions is not possible. Thus IE method has not been practical for the decolorization of textile wastewater.

This study aims to apply IE process with a new regeneration method for the development of practicable safe and cost-effective wastewater reuse options. IE method was applied to remove color and toxicity from Synthetic dyes (Black azo dyes) and biologically treated textile wastewater (BTTWW). Treatment and regeneration performances of enhanced ion exchange system was evaluated by monitoring toxicity (Microtox test), color removal, chemical oxygen demand (COD), and total organic carbon (TOC) parameters.

In the study, a new hydrothermal chlorination method (patent pending) was developed for regeneration and reuse of exhausted anionic resins (Figure 1).

\textbf{Figure 1:} The exhausted anion resin (OH\textsuperscript{-}) before and after hydrothermal chlorination.
Replacing Chloride in Textile Dyeing and the Synergistic Effects on a Hybrid Wastewater Treatment System

M. I. Aydina, A. E. Ateşa, B. Yuzera, Y. Oktema, H. E. Oktenb, H. Selcuk*

Abstract

Dye production wastewaters are known to be non-biodegradable and highly toxic to aquatic environment. Due to intrinsic chemical structures of dyes, the generated wastewater may contain a wide variety of compounds (benzene, naphthalene, anthracene, etc.), bonding groups (amine, carboxyl, sulfonic or their derivatives) and groups (azo, carbon, carbonyl, carbon-nitrogen, sulfur, etc.). Since biodegradation alone was not feasible in effectively treating dyestuff wastewater, advanced oxidation processes (AOPs) have emerged as preliminary stages, where complex nature of the wastewater was simplified and was prepared for the upcoming biological treatment. However, use of AOPs has its own shortcomings. The high chloride content of wastewater that is produced as a result of reactive dyeing, where NaCl is the main electrolyte, can greatly affect homogenous OH radical-based AOPs. Due to initiation and progression of a series of fast reactions by chloride and hydroxyl radical, chlorine/bromine and halogenated organic/inorganic by-products are formed. Halogenated organic compounds that are adsorbable on activated carbon (adsorbable organic halogens - AOX) may form by chlorine reacting with many compounds that are present in dyestuff wastewater. Formation of AOX compounds is quite problematic since it compromises the efficiency of following biological treatment by increasing toxicity and decreasing biodegradability.

In this study, replacement of NaCl with Na2SO4 in reactive dyeing was evaluated in two main aspects: (i) controlling production of toxic and harmful AOX, and (ii) monitoring the effect on anaerobic treatment. Real dye wastewater was obtained from the industry. Two batches of wastewater were prepared in order to simulate chloride-rich wastewater and sulfate-rich wastewater. Both wastewater samples were ozonated for 20 minutes and then optimum time was determined by measuring AOX and toxicity parameters. Optimally ozonated samples were then given to a mesophilic anaerobic reactor, which comprised of three batch reactors in series. Performance of the anaerobic reactor was monitored through measuring parameters of COD, BOD5, NH3 and total gas volume. This study aims to be the pioneer in proposing a change in a textile industry practice in order to produce wastewater streams that can be treated sustainably.

Acknowledgement

The project titled “Investigation of cost effective integrated treatment systems for SETAŞ dye production wastewater” is supported by SETAŞ Kimya Coop. (Çerkezköy, Tekirdağ, Turkey) and Yıldız Technical University Teknopark (DavKeyUpaşa, Istanbul, Turkey). Authors would like to thank TUBITAK for additional support from the project titled “EcosafeFarming - Development and Testing of a Novel Photocatalytic System for Efficient Cogeneration of Clean Water and Hydrogen for Ecosafe Agriculture” No: 117Y194.
Use of Nano Zero-Valent Iron Coated Coffee Grounds Composite for Removal of Zinc and Nickel from Model Electroplating Waste Water

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Keywords: nZVI, Coffee ground, Zinc removal, Nickel removal

Abstract

This research investigates removal capacity of nano zero-valent iron coated coffee grounds (nZVI-CG) as adsorbent material for removal of zinc (Zn) and nickel (Ni). nZVI particles was synthesized and immobilized to the surface of waste coffee grounds using ultrasonic assisted liquid phase method. Synthesized nZVI-CG composite and bare CG particles were characterized using SEM, XRD, TGA, and BET. Batch tests were conducted to elucidate the interaction of parameters such as pH, adsorbent dosage and initial metal concentrations, and their effect on Zn and Ni removal. In kinetic study, reaction time and adsorbent dose were determined as 45 minutes and 1 gr/L, respectively. In solution containing 10 ppm Ni and Zn, removal rates of Zn and Ni were observed as 98.89% and 97.29% for nZVI-CG, respectively; while removal rates of bare CG were remained at 51% and 48.1%, respectively. In conclusion, nZVI-CG composite material is a viable candidate for scaled up Ni and Zn adsorption applications. Hence, the suitability of the adsorbent in Ni and Zn removal at field condition will be tested with a real electroplating waste water in the final part of this study.

1. Introduction

Electroplating, smelting, and metal alloy production generate large volumes of wastewaters with significant concentrations of heavy metals (Li et al. 2017). Nickel and zinc ions usually coexist in high concentrations in electroplating wastewaters. Chemical precipitation, coagulation, ion exchange, adsorption and membrane processes are used for nickel and zinc removal from industrial effluents. However, these processes have several disadvantages such as high capital and operating costs, susceptibility to influent characteristics, operation complexity, chemical sludge production, and low removal efficiency (Li et al. 2017; Harman and Genisoglu 2016). Adsorption is the most popular treatment process due to its removal capacity for a variety of target pollutants, easy operation, and low cost despite low removal kinetics and sensitivity to co-existing pollutants (Harman and Genisoglu 2016). Surface modifications are required to overcome these disadvantages. Immobilization of nZVI on organic and inorganic particulates is a popular research topic in recent years due to superior properties of nZVI such as high surface area and reactivity towards pollutants (Harman and Genisoglu 2016). nZVI coating of sorbent material combines adsorption and oxidation mechanisms. Instant coffee production processes generate huge amounts of coffee grounds as production waste. For the purpose of valorizing a material that is otherwise labelled as waste, coffee grounds are picked as the sorbent material. nZVI coating of coffee grounds (CG) promises a good development in this regard. In this purpose, this study
investigates nickel and zinc removal by a newly developed adsorbent material, i.e. nZVI coated coffee grounds (nZVI-CG).

2. Materials and Methods

2.1. Materials and Chemicals

Analytical grade chemical reagents namely, zinc nitrate hexahydrate [Zn(NO₃)₂.6H₂O], nickel nitrate hexahydrate [Ni(NO₃)₂.6H₂O], sodium borohydride [NaBH₄], ferric chloride [FeCl₃], absolute ethanol [C₂H₆O], sodium hydroxide [NaOH], and hydrochloric acid [HCl] were used in this study. All solutions were prepared daily, using deionized water (resistivity 18.2 MΩ·cm). The pH was adjusted by using 0.1 M sodium hydroxide [NaOH] or 0.1 M nitric acid [HNO₃]. Waste coffee ground (CG) particles were used as adsorbent material.

2.2. Preparation of nZVI Particles

Coffee grounds were reduced in particle size (d<63 μm). In order to increase the efficiency of coating, coffee grounds were put in acid solution. Acid activation was done by soaking particles in 1M HCl and stirring intermittently for 24 hours. At the end of 24 hours, particles were washed with deionized water until pH was stabilized at 4 in order to inhibit the leaching mechanism. Acid activated particles were dried in order to prepare for coating with nZVI. Coating procedure was applied following the protocol given at Liu et al. (2014). CG-nZVI was synthesized according to general liquid phase method in which coffee grounds were used as support material, and iron ions (FeCl₃) were reduced by borohydride (NaBH₄) (Shi et al. 2011, Uzum et al. 2009, Liu et al 2014, Ponder et al. 2000). 3 gr of coffee grounds were taken into a three-necked volumetric flask and then 50mM FeCl₃ solution was poured in. After mixing for one hour, freshly prepared NaBH₄ solution (100 mL DDI within the 0.95 gr NaBH₄) was added drop by drop (50-60 drop/min) and mixed for 60 minutes. 37 kHz sonification was applied in order to keep solution homogenous. Synthesis processes were conducted under nitrogen atmosphere. CG-nZVI was separated from solution by centrifuging at 8000 rpm for 10 minutes. Then, CG-nZVI was dried overnight in a porcelain crucible at 65 °C. Dried CG-nZVI was kept at tightly capped amber bottles until use in order to prevent oxidation.

2.3. Characterization studies

Surface morphologies of CG and CG-nZVI particles were analyzed with SEM coupled with EDAX and EDX systems. All samples were coated with gold (Au) with ion spray device prior to SEM analysis. Images of coated particles and outer surface of the support material were obtained, and also EDX scan results were acquired. Chemical composition analyzes were performed on XRD spectroscopy. CG and CG-nZVI surface areas were determined by BET adsorption method and thermal stabilities were determined using a thermogravimetric analyzer (Diamond TG/DTA, PE).

2.4. Removal of Nickel and Zinc

Zn and Ni removal experiments were carried to investigate effects of initial Zn and Ni concentration (5, 10 and 15 mg/L), adsorbent type (CG-nZVI vs CG) and solution pH (3, 5, and 7) on removal efficiency. CG and CG-nZVI particles were added to 100 mL solution with selected initial metal concentrations and initial pH values. While the mixtures were stirred at 250 rpm continuously, temperature was kept at 25 °C. At certain time intervals, samples were taken and filtered to remove particles. Then, residual concentrations of Ni and
Zn were measured by using Inductively Coupled Plasma (ICP-MS, Agilent 7500). In addition, a kinetic experiment was done in order to determine the optimum reaction time.

3. Results

3.1. Characterization of CG and CG-nZVI

The morphology and structure of CG and CG-nZVI particles were characterized by SEM. The SEM images of CG and CG-nZVI are shown in Figure 1. Surface of original CG was smooth and had an irregular multilayer lamellar structure. Modified CG-nZVI particles were spherical in shape.

![SEM images of CG (left) and CG-nZVI (right).](image)

Figure 1. SEM images of CG (left) and CG-nZVI (right).

3.2. Effect of pH on Ni and Zn removal

pH of the solution is one of the most important operating parameters which plays an important role in metal removal. It influences distribution of metal species and surface features of adsorbents. Three pH values (3, 5 and 7) were investigated for nZVI and CG-nZVI (Figure 2). Ni and Zn removal efficiencies increased with solution pH and reached maximum at pH 7. At initial metal concentration of 10 ppm, Ni and Zn removal efficiencies were found as 48% and 51% for CG particles, respectively. On the other hand, Ni and Zn removal efficiencies were 97.29% and 98.89% for CG-nZVI particles, respectively. Considering these results, pH of solution was kept constant at pH 7 while investigating the effect of initial metal concentration.
3.3. Effect of initial metal concentration on Ni and Zn removal

Figure 3 shows the effect of initial metal concentration on the removal of Ni and Zn using nZVI and CG-nZVI particles. It was observed that the removal efficiency decreased with increasing initial metal concentration for CG particles. The removal efficiencies for Ni and Zn is almost 90% at initial metal concentration of 5 ppm. Afterward the removal efficiency decreased considerably with the increasing both Ni and Zn initial concentrations. On the other hand, the removal efficiency reached almost 90% for 5 and 10 ppm Ni and Zn initial concentrations using CG-nZVI particles. At 15 ppm Ni and Zn initial concentration, the CG-nZVI particles presents better removal efficiencies than CG particles.
Figure 3. The effect of metal concentration on Ni and Zn removal for CG and CG-nZVI.

References


Life Cycle Assessment of Hydrogen-based Electricity Generation in place of Conventional Fuels for Residential Buildings

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Keywords: Hydrogen, life cycle assessment, environmental impact, global warming, NOx, SO2.

Abstract

In this study, an environmental impact evaluation of electricity generation processes driven by conventional fuels and hydrogen is carried out with a life cycle assessment (LCA) for residential uses. For this purpose, lignite, natural gas, and hydrogen are utilized to a power plant to generate electricity. The present results show that global warming potentials for each fuel were found as 181 ton CO2 eq, 80 ton CO2 eq and 6 ton CO2 eq, respectively.

1. Introduction

In 2017, 37% of electricity generation in Turkey has been obtained from natural gas, 33% from coal, 20% from hydraulic energy, 6% from wind, 2% from geothermal energy and 2% from other sources (Ministry of Energy and Natural Resources, 2018). However, fossil fuel use causes hazardous emissions to the environment. The most important impacts on the environment which should be investigated are global warming, acid rains, and ozone layer depletion. Global warming is mainly occurring due to the warming effect of CO2 and the acid rains mostly depend on NOx and SO2 emissions. On the other hand, NOx has some huge impact on the depletion of ozone in the stratosphere (Dincer et al., 2009).

Note that a total of 22% of the produced electricity is consumed in the residential buildings in Turkey (Tuik, 2016). Therefore, the reduction of the fossil fuel usage at the buildings provides reducing of environmental impacts, significantly. For this reason, hydrogen energy has been studied by many researches (Ebaid et al., 2015; AlRafea et al. 2016). Lubis et al. (2009) investigated the utilization of hydrogen energy in the residential buildings in Canada and show that it decreases the global warming impact of the country.

The purpose of this study is to investigate the hydrogen solution for electricity supply to 50 residential houses in Turkey and show that hydrogen has the lowest impact to the environment according to natural gas and lignite that is used currently for this purpose.

2. Materials and Methods

An LCA study is conducted with Simapro software (Simapro, 2012) for the system shown in Figure 1.
The environmental impact assessment studies are undertaken with the CML 2001 method. The fuels, such as natural gas, lignite, and hydrogen are considered as they are utilized in the thermal power plants as fuels to generate the electricity. The environmental impact assessments are performed in this regard for comparative evaluations.

3. Results

The results of LCA show that hydrogen offers the best solution with the minimum global warming potential, NO\textsubscript{x} and SO\textsubscript{2} emissions as seen from Figures 2 and 3. However, lignite causes the most hazardous effects on the environment during the electricity generation in the power plant. The highest NO\textsubscript{x} and SO\textsubscript{2} emission values were found as 155 kg NO\textsubscript{x} equivalents and 178 kg SO\textsubscript{2} equivalents for the lignite-based generation of electricity.

![Figure 1. Schematic diagram of electricity generation and distribution to residential buildings](image1)

Figure 1. Schematic diagram of electricity generation and distribution to residential buildings

![Figure 2. The variation of global warming potential with fuel used in power plant](image2)

Figure 2. The variation of global warming potential with fuel used in power plant

![Figure 3. The change of Sulphur dioxide and Nitrogen oxides during electricity generation with different fuels](image3)

Figure 3. The change of Sulphur dioxide and Nitrogen oxides during electricity generation with different fuels
References


Estimation of the air pollutants exposure and GHG emissions from the road transport in an urban area

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Keywords: commute, exposure, black carbon, particle matter.

Abstract

In urban areas where traffic intensity is high, people are exposed to traffic sourced emissions when traveling during various daily activities. Within this study, the exposure concentrations and inhalation doses of BC, UFP and PM₂.₅ were determined for different travel modes (bus, metro-bus and car) and four different routes in Istanbul. Additionally, the greenhouse gas emissions (GHG) were calculated for each travel mode and for different routes. The metric GHG values of commuters was determined for different road transport modes.

1. Introduction

In urban areas, transportation vehicles are a significant source of many air pollutants and also a major contributor to the greenhouse gas emissions. The United Nations Framework Convention on Climate Change (UNFCCC) stated that the 72% of the GHG emissions produced by transport sector in the worldwide are caused by the road transport (UNFCCC, 2015).

2. Materials and Methods

We measured UFP, BC and PM₂.₅ concentrations using personal air samplers, during the period of June 2016 to September 2017, in different transport microenvironments (bus, metro-bus and car). The measurements were done by the portable equipments. UFP measurements between 10 nm-1000 nm, were made with the particle counter (TSI 3007 Hand held Condensation Particle Counter). BC measurements were made by MicroAeth AE51. PM₂.₅ measurements were made by Thermo PDR 1200 that works according to the light scattering method. We considered two conditions during in car measurements (1) windows down and air vent circulation off (2) windows up and air vent circulation was set at moderate, air conditioning (A/C) on. The CO₂ emissions emitted by different road transport modes were calculated using by EMEP/EEA emission factors and carbon footprint of the commuters were determined for each trip (EMEP/EEA, 2016).

3. Results

Table 1 shows exposure concentrations and inhalation doses of BC, UFP, PM₂.₅ and emission of CO₂ for different travel mode. The average BC, UFP and PM₂.₅ concentrations were 11.1 μg/m³, 33342 pt/cm³, 40.3 μg/m³ in bus and 9.5 μg/m³, 31622 pt/cm³, 21.9 μg/m³ in metrobus, respectively.
Table 1. The exposure concentrations and inhalation doses of BC, UFP, PM₂.₅ and emission of CO₂ for different travel mode.

<table>
<thead>
<tr>
<th>Commute mode</th>
<th>Emission of CO₂ (kg)</th>
<th>In vehicle concentration</th>
<th>Exposure</th>
<th>Personal CO₂ emission of trip</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>BC (μg/m³)</td>
<td>PM₂.₅ (μg/m³)</td>
</tr>
<tr>
<td>Bus1</td>
<td>30144</td>
<td>32795±14973</td>
<td>11.2±7.0</td>
<td>37.1±16.7</td>
</tr>
<tr>
<td>Bus2</td>
<td>15072</td>
<td>33689±13991</td>
<td>11.1±5.9</td>
<td>43.4±35.0</td>
</tr>
<tr>
<td>Metrobus1</td>
<td>22608</td>
<td>36969±12732</td>
<td>10.4±4.8</td>
<td>26.7±15.0</td>
</tr>
<tr>
<td>Metrobus2</td>
<td>31651</td>
<td>26275±11099</td>
<td>8.6±4.6</td>
<td>17.1±11.7</td>
</tr>
<tr>
<td>Car (Windows open)</td>
<td>6678</td>
<td>63825±19777</td>
<td>18.2±7.8</td>
<td>35.7±15.9</td>
</tr>
<tr>
<td>Car (Windows close)</td>
<td>7224±4696</td>
<td>2.3±1.3</td>
<td>8.3±5.8</td>
<td>1.4E+4±0.9E+4</td>
</tr>
</tbody>
</table>

The BC, UFP and PM₂.₅ concentrations measured in car during windows down was found 7.9, 8.8 and 4.3 times higher than measured in car during windows up, respectively. The inhalation doses were determined as 0.36-0.24 μg/km for BC, 10.8E⁺⁸-8.1E⁺⁸ pt/km for UFP and 1.33-0.56 μg/km for PM₂.₅ in bus and metrobus. It was observed that the BC, UFP and PM₂.₅ exposures in car (windows open) were 0.36 μg/km, 12.6E⁺⁸ pt/km and 0.70 μg/km, respectively, while the windows up, we observed that BC was 0.04 μg/km, UFP was 1.4E⁺⁸ pt/km and PM₂.₅ was 0.16 μg/km.

References

Acknowledgement
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Reduction of VOC in Workplace Indoor Air With Ozone Application

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Keywords: Ozone, VOC, Indoor Air

Abstract

In this study, volatile organic compounds (VOCs) removal efficiency with ozone application was investigated. Within this aim, a solvent used in a button production plant was used as VOC source. The experimental study was conducted in an airtight room and the VOC removal with ozone application was investigated for different test conditions.

1. Introduction

Pollutants emit many sources of indoor air and cause health problems. In particular, materials used in some industrial processes increase the concentration of volatile organic compounds. VOCs need to be eliminated because of the limit values brought by the regulations on occupational health.

2. Materials and Methods

Work was carried out in a fixed closed cabin (60cm x 80cm x 80cm). The VOC value in the cabin was monitored continuously by Honeywell GasalertMicro 5 PID device, while air conditioning conditions (CO\(_2\), Temperature, Humidity, Pressure, Air Flow Rate) were continuously monitored with Testo 480 Device. Ozone application was performed by using Ozonmatik Portomatic Multi Device. In this study, VOC formation amount and speed of solvent were investigated under closed conditions. Each experiment was repeated 3 times for similar conditions. After a certain period of time, 30 mg and 60 ppm fixed VOC concentrations of 16 mg (2 min), 32 mg (4 min) and 62 mg (8 min) ozone were compared by removing the yield.

3. Results

Figure 1 shows graphs showing the decrease in VOC levels if different ozone levels are applied in the cabinet with 30 and 60 ppm VOCs. The highest VOC reduction was achieved when ozone was given for 8 minutes with 33-55%.

It has been observed in the trials that the application of ozone to the environments with low VOCs can reduce the VOC in the environment by half. According to the results of air conditioning measurements, the application of ozone increases the CO\(_2\) level in the environment by 5 ppm (2 min ozone application) and 20 ppm (8 min in ozone application). Before and after the ozone administration, VOCs were sampled in activated carbon tubes under stable conditions and analyzed by GC-MS. Styrene constitutes 99% of the total VOC. It was observed that approximately 21% of total styrene was removed by ozone application. However, benzene concentration at the level of 3-5 µg/m\(^3\) increased by 1200 µg/m\(^3\) with ozone application in the environment.
Figure 1. VOC removal efficiencies when ozone applied.
Composting of Sludge by Soil Worms and Monitoring of Vermicompost Quality

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Keywords: Sewage sludge, Industrial sludge, Vermicompost, \textit{Eisenia fetida}

Abstract

In this study, carried out in 3000 g composting containers under open test conditions, domestic and industrial sewage sludge incubated by soil worms (\textit{Eisenia fetida}) and vermicompost produced. For this purpose; domestic and industrial sewage sludge were incubated with manure at 5\%, 10\%, 15\%, 20\% and control. The change in quality parameters monitored such as pH, electrical conductivity, humidity, total nitrogen, total organic carbon and C/N by taking samples from the vermicompost obtained on day 1, day 30, day 60 and day 90 during the times of incubation. When the results of study were examined, statistical difference ($P<0.05$) was observed between vermicompost quality parameters and domestic/industrial sludge. While there was no significant difference between the administration doses, the difference between the incubation times found to be significant.

1. Introduction

Vermicompost can be used in the safe management of waste of agricultural industry, domestic and hospital that constitutes a serious threat to life and the environment, due to its natural, biological, biochemical and physicochemical properties (Borah et al., 2007). In the recovery of domestic and industrial organic waste, vermicompost has superior properties than aerobic compost in both process and product (Dominguez et al., 1997). Vermicompost fertilization has been found to increase plant growth and soil fertility in many studies so far (Atiyeh et al., 2000; Arancon et al., 2005; Azarmi et al., 2008). Industrial wastewater treatment sludges incubated with \textit{Eisenia fetida} type worms for 9 weeks and compared with the treatment sludge without worms (Parvaresh et al., 2004).

2. Materials and Methods

Wastewater Treatment Plant Sludge of Tekirdağ (TESKİ) and industrial sludge (a textile plant) used as the material. Certain amounts of sewage sludge and manure have been made with vermicompost in the composting container. 15 unit soil worms (\textit{Eisenia fetida}) were left in each composting container. Trial applied to be as 2 different treatment sludge x 1 kinds of fertilizer x 4 sludge doses = 8 composting container. Each compost sampled at 4 periodic days (1st, 30th, 60th, 90th day). 32 samples were taken in the experiment. Electrical conductivity (EC), pH, moisture, total nitrogen (TN), total organic carbon (TOC) analysis performed according to standart methods (TS EN). Statistical analyzes performed using SPSS program.
3. Results

The mean values of pH, EC, humidity, TOC in both sludge were limit values and TN, C/N were found above limit values. Accordingly, the lowest C/N observed in 15% domestic sludge application and the highest C/N observed in 20% domestic sludge application (Table 1).

| Sludge | Mean ± SD | P(%) 
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>Doses</td>
<td>Domestic</td>
<td>12.5 ± 5.7</td>
</tr>
<tr>
<td></td>
<td>Industrial</td>
<td>12.5 ± 5.7</td>
</tr>
<tr>
<td>pH</td>
<td>Domestic</td>
<td>7.0 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>Industrial</td>
<td>7.2 ± 0.3</td>
</tr>
<tr>
<td>EC</td>
<td>Domestic</td>
<td>1.76 ± 1.08</td>
</tr>
<tr>
<td></td>
<td>Industrial</td>
<td>2.10 ± 1.06</td>
</tr>
<tr>
<td>Humidity</td>
<td>Domestic</td>
<td>41.8 ± 23.6</td>
</tr>
<tr>
<td></td>
<td>Industrial</td>
<td>42.9 ± 24.4</td>
</tr>
<tr>
<td>TN</td>
<td>Domestic</td>
<td>8.2 ± 4.7</td>
</tr>
<tr>
<td></td>
<td>Industrial</td>
<td>9.9 ± 5.5</td>
</tr>
<tr>
<td>TOC</td>
<td>Domestic</td>
<td>29.2 ± 24.9</td>
</tr>
<tr>
<td></td>
<td>Industrial</td>
<td>31.3 ± 25.4</td>
</tr>
<tr>
<td>C/N</td>
<td>Domestic</td>
<td>35.5 ± 19.2</td>
</tr>
<tr>
<td></td>
<td>Industrial</td>
<td>34.6 ± 22.4</td>
</tr>
</tbody>
</table>

Table 1. The Effect of domestic and industrial sludges on vermicompost quality parameters (independent sample t test)

References


Development of a New Integrated Textile Wastewater Treatment and Hydrogen Production System with Ion Exchange Membranes

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Keywords: Hydrogen production, textile wastewater, ion exchange membranes.

Abstract

Bipolar membranes have been used for many years to generate organic and inorganic acid, base and desalinated fresh water in various industries. A bipolar membrane is generally composed of anion- and cation exchange membrane layers and can split water at the junction point of these membranes into hydrogen ion and hydroxyl ion under the applied electrical field. The electrodialysis process with the bipolar membrane (BPMED) is a proven technology for the treatment of textile wastewater with high salt concentration (40-80 g/L) while producing acid and base \cite{1}. However, a high dye concentration content of textile wastewater causes fouling to the membranes and decreases the ion transfer efficiency of the bipolar membrane electrodialysis process. The color of the wastewater should be removed before the BPMED process to prevent membrane fouling. The hardness of the wastewater is considered another problem that causes membrane fouling in the BPMED system, and it has to be removed before the BPMED process. Since many studies reported different color removal methods \cite{2}, ion exchange process is an effective and cost-saving treatment method prior to the BPMED process. The strong base anion exchange resins are capable of removing dye solution from wastewater while releasing Cl$^-$ and OH$^-$ ions into the wastewater \cite{3}. Also, other anions that might be present in the content of the wastewater can easily be removed. In this way, the possibility of contamination of the produced acid can be prevented. The other advantage of the anion exchange process is the ability of hardness removal from wastewater with the precipitation of Ca$^{2+}$ and Mg$^{2+}$ by the help of OH$^-$ ions that are released from ion exchange resins.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Water splitting hydrogen production cell with bipolar membrane.}
\end{figure}
Hydrogen is an environmental-friendly alternative fuel source which can potentially be used in various industries as gas or liquid. The water electrolysis is known as the most common hydrogen production method that decomposes the water into hydrogen and oxygen gas. The electrolysis process is composed of anode and cathode compartments. The placement of the bipolar membrane between anode and cathode side will increase the pH of anolyte and decrease the pH of catholyte (Figure 3) while producing hydrogen gas at the cathode side and oxygen gas at the anode side [4]. This change in pH can increase the hydrogen production efficiency and decrease the required energy consumption.

![Figure 4: Integrated hydrogen production and textile wastewater treatment system flow diagram.](image)

In the present study, an integrated hydrogen production and the treatment of textile wastewater is investigated conceptually and experimentally with an aim to achieve zero waste discharge (Figure 4). The textile wastewater is treated with a strong base ion exchange resin inside the ion exchange column to remove the color of the wastewater. Also, after the ion exchange process with the increase in pH of the textile wastewater is resulted in a decrease of the hardness causing ions (Ca$^{2+}$ and Mg$^{2+}$) concentration. After ion exchange process, the hydrogen gas is generated from the textile wastewater by using the bipolar membrane in the electrolysis process. Finally, the textile wastewater is treated with the BPMED process to remove salt from the wastewater while producing acid, base and clean water that can be reused in the wet textile processes. Numerous performance parameters, such as current efficiency, limiting current efficiency, current utilization efficiency, hydrogen production efficiency, and the water quality parameters, such as color, conductivity, absorbance, pH, chemical oxygen demand (COD), etc. are monitored while running all integrated processes. It can be concluded that the proposed hydrogen generation and wastewater treatment system is a promising method that can generate hydrogen while treating the wastewater.

References

Economic Analysis and Design of A Hybrid Autonomous Floating Photovoltaic-Fuel Cell System integrated with A Hydrogen Production Unit

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Keywords: Floating photovoltaic, Hydrogen fuel cell, Energy storage

Abstract

This study deals with the intermittent availability and land occupation problems of conventional photovoltaic (PV) power plants. Hydrogen production and accumulation units have been integrated as an energy storage system. Floating application of the photovoltaic power plant has been investigated for land conservation purposes. Meteorological and other data is taken from Kilicli Pond (Kılıçlı Göleti), Mediterranean Region, Turkey. Photovoltaic system has been simulated in the PvSyst Software. Furthermore, HOMER Pro Software has been employed for analysis and simulation of whole system with the obtained results from PvSyst Software. A small community with a 94.48 kWh/day average electric demand is supplied by stand-alone floating PV-fuel cell (FC) hybrid electric production system. According to PvSyst results, 63.0 kWp floating PV system produced 94.49 MWh/year electricity. Also, 2.86 kg/day average hydrogen consumption in Fuel cell is supplied from a stored hydrogen reservoir which is produced via electrolyzer. The whole system brings an autonomous power generation to the community which is a crucial matter for the regions far from power distribution network. During the year, 1046 kg hydrogen and 111 896 kWh electricity has been produced at levelized cost of electricity (LCOE) $0,615/kWh.

1. Introduction

The population increase and industrialization reveals a growing energy demand. Currently fossil fuels are leading and dominating the energy generation globally. But the fossil fuel combustion is major contributor to the climate change and pollution (Perera et al. 2018). Photovoltaic systems are one of the most competitive renewable energy alternative. But they are insufficient to cover most type of electrical demands stand-alone. In that matter, hydrogen based energy storage systems are alternative solution. The production methods of hydrogen is investigated. Solar based hydrogen production is compared with other methods both environmentally and economically (Dincer, 2012). Solar based hydrogen production systems, essential implementations and education program is investigated with economic forecast (Nowotny, Veziroglu et al., 2014). Exergoeconomic analysis has been studied for flat plate solar collector in an integrated system for hydrogen production. Multi objective optimization is performed for enhance the exergy efficiency (Khanmohammadi et al., 2017). Floating photovoltaic applications are potential solution for land conservation. The first application had been installed for research purposes in Aichi, Japan in 2007. After that the first commercial floating PV plant is built on behalf of Far Niente wineries by SPG Solar in California, USA. (Trapani et al., 2015). Floating systems are also conserving the water resources through shading the water and reducing the evaporation. According to research in Australia, %40 of the water could lost through evaporation (Craig et al., 2005).
2. Materials and Methods

The autonomous power generation system includes, floating photovoltaic system, electrolyzer, hydrogen fuel cell and hydrogen tank [Fig.1.].

![System configuration. (HOMER Pro Software)](image)

Electric supply for small community has been analyzed in HOMER Pro Software. Separately, floating pv system has been simulated in PvSyst software. In addition to softwares, direct mathematical approach is used in order to determine economic viability.

3. Results

According to the PvSyst simulation, 63.0kWp floating PV power plant produced 94 493 kWh/year electricity. This result is used in Homer Pro software. With the electric load and PvSyst result, system has been sized in most feasible way which shown in Table 1.

![Table 1. Feasible component sizes obtained in HOMER Pro Software.](image)

Floating application brings major and minor enhancements to the photovoltaic power plant. Efficiency of electricity generation has been increased through operating temperature decreasing. Depending on temperature coefficient of the PV panel, around 4 °C operating temperature decreasing lead to around 1.58% electricity generation efficiency(Liu et al., 2017) The electrolyzer operated 3003 hours in a year. Total electricity consumption of the Electrolyzer is 48.55 MWh/year at specific consumption 46.4 kWh/kg-hydrogen. Electrolyzer produced 1046 kg hydrogen for a year. The size of the hydrogen tank is determined to be 30 kg and total energy capacity is 1000 kWh. Total fuel consumption is 1044 kg/year. Total electricity production of the system that is 111.94 MWh/year at 0.6124 $/kW LCOE. The Fuel Cell generated 17.40 MWh/year, representing 15.6% of the total production and the Floating PV System’s production is 94.49 MWh/year which is equal to 84.4% of the total production.
FPV System (PVsyst) was generally active between 06:00 -18:00 and fuel cell operated generally after 18:00 to 06:00. Total unmet electric load is 0.29 MWh/year which represents only 0.843% of the total electricity load. Excess electricity is 29.15 MWh/year.

References


Assessment of Net Additions to Stock and Embodied Energy for Eryaman District, Turkey via 3D GIS

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Keywords: Urban metabolism, construction material stock, Net addition to Stock, NAS indicator, Material Flow Analysis embodied energy.

Abstract

Construction material needs and associated solid waste potential of the built-in environment is one of the important issues of urbanization. Energy needed to produce these construction materials comprise an important share of total energy requirement of the society. Promotion of transition to more environmentally conscious construction materials including the use of natural, local and recyclable material consumption is important for both energy demand and solid waste management given the expected increase in urbanization in the near future.

In parallel to global trends, urbanization has been increasing in cities of Turkey that are characterized by high industrial production and growing services and tourism sectors. Ankara is one of these cities that experienced exponential growth of the built-in environment in recent years. This study estimated the change in Net Additions to Stock (NAS) indicator of a pilot area of 7.34 square kilometers in Eryaman district, Ankara between 1998 and 2015. For this purpose, orthophoto images of the area, ready-to-use maps and Digital Elevation Model (DEM) for the year 2015 were compiled and processed using NETCAD. The results showed that there was a 26% increase in the built-in environment from 1998 to 2015. The material stock increased from 7,81 megatons in 1998 to 9,83 megatons in 2015 of which 7,68 megatons comprise of recyclable materials. Embodied energy due to the use of construction materials also increased significantly by 26% from 1998 to 2015. The results enabled quantification and a better understanding of the scale of solid waste potential and energy requirement of Eryaman district that has urbanized at a rapid rate from 1998 to 2015. Given the expected increase in urbanization in major cities of Turkey, proactive policies needs to be developed for solid waste management.

1. Introduction

Rapid urbanization in cities has resulted in many environmental impacts that range from changes in hydrologic cycle to increase in ambient temperatures with adverse effects on ecosystem and public health. One of these problems is the need for construction materials and accompanying need for solid waste management at the end-of-life of buildings along with the need for materials to meet the needs of the urban population. The scale and trend of growth and the change in factors that affect the growth should be monitored for effective solid waste and energy demand management in cities.

Urban metabolism studies enable a better understanding of consumption patterns of cities and their progress over time. Urban metabolism identifies the inputs required for the functioning of a city, the data on accumulations in the system and outputs of the system are...
collected in a certain systematic way and the indicators specific to the metabolism are calculated. One of the indicators of urban metabolism is Net Addition to Stock (NAS) that refers to the transformation of inputs and the material and energy stored in the system after the outputs are removed from the system. NAS indicator is indirectly a measure of the economic growth of the urban area. Direct and indirect Material Flow Analysis methods can be used to evaluate NAS for a particular city.

Urbanization in many cities of Turkey has an upward trend. Among these cities Ankara is one the cities that has a large number of buildings due to rapid increase of urbanization specifically for some districts such as Eryaman and Çankaya. This study assessed the change in material stock of a pilot urban area, 7.34 square kilometers of Eryaman district, Ankara between 1998 and 2015 using GIS data of the region. Material stock per capita for Ankara was then calculated and compared with that of other cities in Europe by extrapolating the results based on population densities of the pilot area and Ankara. Recyclability potential of the materials and embodied energy were also quantified.

2. Materials and Methods

Orthophoto images, ready-to-use maps (maps that contain area of buildings as well as their elevation data) and point cloud produced from Digital Elevation Model (DEM) of the pilot area were used to identify the type of buildings in the pilot area and quantify material stock. Figure 1 and 2 present orthophoto image and point cloud for the region. For each type of building, data on composition of materials were compiled by two construction engineer experts based on regulatory specifications for each type of building. Embodied energy was calculated using data from ICE database that contains embodied energy and carbon data for construction materials (ICE, 2018). Embodied energy is the amount of energy consumed to extract, refine, process, transport and produce a material or a final product.

Figure 1. An orthophoto image from the pilot area: Eryaman District, Ankara

Figure 2. Point cloud of the pilot area produced from Digital Elevation Model (DEM)
3. Results

Table 1 presents the change in type and number of buildings between 1998 and 2015. In 1998, of the 7.34 km² of total study area, 4.59 km² was built-in environment with a material stock of 7.8 megatons. In 2015, material stock increased to 9.8 megatons for a built-in environment of 5.8 km². Table 1 presents the change in type and number of buildings between 1998 and 2015.

**Table 1. Type and number of buildings for the year 1998 and 2015**

<table>
<thead>
<tr>
<th>Type of building</th>
<th>Number of buildings (1998)</th>
<th>Number of buildings (2015)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brick masonry with ceramic tile</td>
<td>622</td>
<td>622</td>
</tr>
<tr>
<td>Brick masonry with membrane tile</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>Concrete building with ceramic tile</td>
<td>573</td>
<td>599</td>
</tr>
<tr>
<td>Concrete building with membrane tile</td>
<td>1,778</td>
<td>2,107</td>
</tr>
<tr>
<td>Mosque</td>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>Brick masonry without a roof</td>
<td>21</td>
<td>23</td>
</tr>
<tr>
<td>Total</td>
<td>3,008</td>
<td>3,369</td>
</tr>
</tbody>
</table>

Following identification of material composition for each type of building, material stock per capita for the region was calculated. 23 different types of materials were identified including aluminium, PVC, copper, clay and EPS. Extrapolation of the results of the pilot area based on population densities of the pilot area and Ankara, Net Additions to Stock (NAS) for the city of Ankara was found as 72 ton/capita for the year 2015. This result is higher than that of Lisbon with a NAS of 15.7 ton/capita (Rosado et al., 2014) whereas it is less than Vienna’s NAS of 210 ton/capita (Kleemann et al., 2016).

The total embodied energy for 1998 and 2015 were found as 16,756 TJ and 21,161 TJ, respectively. The amount of embodied energy for residential buildings per square meter was found as 3,6 GJ. This value is close to the lower limit of the range of 3-8 GJ noted previously in the literature (Atmaca 2016). Embodied energy due to the use of construction materials increased significantly by 26% from 1998 to 2015. The results enabled quantification and a better understanding of the scale of solid waste potential and energy requirement of Eryaman district that has urbanized at a rapid rate from 1998 to 2015. Given the expected increase in urbanization in major cities of Turkey, proactive policies needs to be developed for solid waste management.

References

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POSTER PRESENTATIONS
Determination of Transport Coefficients of Inorganic Contaminants Through Alternative Liner Systems from Leachate to Groundwater Using One-Dimensional Mass Transport Model

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Keywords: 1-D mass transport model, Inorganic contaminant transport, Heavy metals, Inorganic macrocomponents, Leachate, Liner systems

Abstract

In the present study one-dimensional (1D) advection–dispersion transport modeling was conducted for evaluation of inorganic (heavy metals and inorganic macrocomponents) contaminant transport through alternative liner systems from leachate to groundwater. Ten identical pilot-scale landfill reactors with different alternative composite liners were operated for a period of about 290 days and transport coefficients of heavy metals and inorganic macrocomponents were determined. Results of the study showed that Pb had the highest dispersion coefficient (48.77 × 10⁻⁸ m²/s) whereas Ni had the lowest dispersion coefficient (2.07 × 10⁻⁸ m²/s) among all heavy metals and K had the lowest dispersion coefficient (1.5 × 10⁻⁸ m²/s) among inorganic macrocomponents. The results obviously indicated that the transport of inorganic compounds to the groundwater can be noticeably decreased with the particular use of bentonite and lime materials in composite liner systems. Utilization of lime prevented heavy metal transport by increasing pH values, thus increasing adsorption capacity of the liners and increasing precipitation ratio of the heavy metals.

1. Introduction

Municipal solid waste (MSW) landfills pose an environmental threat to groundwater resources due to leachate migration. Leachate is highly contaminated and complex structured wastewater consisting of a wide range of toxic inorganic and organic compounds. Pollutants in MSW landfill leachate can be divided into four groups: dissolved organic matter that can be measured as chemical oxygen demand (COD), biochemical oxygen demand (BOD); inorganic macro components; heavy metals; and xenobiotic organic compounds [1]. The major sources of heavy metals in landfills are the co-disposed industrial wastes, incinerator ashes, mine wastes and household hazardous substances such as batteries, paints, dyes, inks, etc. [2, 3]. Soils have been contaminated with heavy metals such as lead, copper, zinc, iron, manganese, chromium, and cadmium leading to serious problems because heavy metals are unbiodegradable contaminants.

Liner system is one of the most important elements of a modern engineered landfill [4]. The effectiveness of modern landfill liner systems to minimize migration of organic and inorganic contaminants is of great concern. Composite liners consisting of a geomembrane (usually high density polyethylene (HDPE) 1–2.5 mm-thick) overlying a compacted soil liner (0.30–1.5 m-thick) are the standard design for liner systems in municipal solid waste
landfills [5]. Alternative liners are permitted, provided that they are shown to be equivalent to the standard composite liner and in some cases these liners are more effective at preventing groundwater contamination. Popular alternatives are to replace compacted soil liner with a low-cost natural materials or to utilize some materials to decrease hydraulic conductivity of the liner material and avoid contaminant transport. More recently, alternative liner materials have been proposed as a replacement for all or part of the clay component of composite liners, although little field evidence exists regarding their effectiveness at limiting contaminant migration.

The predominant pathways for solute transport through composite liners depend on the type of contaminant; (1) inorganic and organic solute transport through defects in the geomembrane and subsequently through the soil liner by advection and dispersion, (2) transport of organic solutes through the intact geomembrane and subsequently through the soil liner by diffusion (contaminant migration driven by the difference in concentration between the upper and lower sides of the liner) [5 - 8]. Since geomembranes are essentially impervious to diffusion of inorganic solutes [9] and liquid flow [5, 10, 11], the predominant pathway for transport of inorganic solutes is through defects in the geomembrane. Then the solute is transported through the soil liner and underlying soil layers via advection, diffusion, or a combination thereof [7].

Flow and solute transport through composite liners are three-dimensional processes. The approach used herein is to analyze a one-dimensional system that approximates the characteristics of the three-dimensional system. In this paper, an analytical solution of 1D contaminant transport through alternative composite liner systems was presented under conditions of steady-state flow and transport parameters (dispersion coefficients) of inorganic contaminants were determined. The performance of different liner systems were evaluated by the systematic and comprehensive approach.

2. Materials and Methods

2.1. Reactor setup and operation

Ten pilot-scale landfill reactors (R1-R10) were operated for about 290 days to investigate advective transport of heavy metals representing inorganic contaminants. All parts of the reactors were made of HDPE pressurized pipes with a wall thickness of 0.005 m. The diameter (DR) and height (HR) of the reactors were 0.40 m and 0.80 m, respectively. The diameter and the height of the reactors made of HDPE pressurized pipes were 40 cm and 80 cm, respectively. The reactors were comprised from two parts; consisting leachate in the upper part and distilled water simulating groundwater in the lower part. The bottom of the both parts of the reactors consisted of perforated pipes inserted to collect samples from leachate and groundwater.
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October 24-26, 2018 - Istanbul / TÜRKİYE

Figure 1. Schematic presentation of the experimental set-up

References


Treatment of Tannery Industry Wastewater by Electrocoagulation Process Using Iron Electrodes

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Keywords: Tannery industry wastewater, electrocoagulation, iron electrodes, cost

Abstract

This work deals with investigation of electrocoagulation process for tannery industry wastewater treatment. The removal of COD, TSS and color from tannery wastewater was experimentally investigated using iron electrodes. Effects of initial pH, electrolysis time and current were examined. Optimum values of operational parameters were experimentally determined for maximum COD, TSS and color removal. The batch experimental results revealed that COD, TSS and color removal efficiencies were 75, 98 and 99 % under optimum conditions (pH: 7, electrolysis time: 60 min, current: 3 A). Operational cost are calculated as 6.80 €/m³ for optimum conditions. The results of the experimental study showed that the electrocoagulation process using iron electrodes is an effective treatment method for tannery wastewater.

1. Introduction

The tannery industry is one of the industries with high water consumption. The tannery industry wastewater includes high levels of salinity, organic pollution, inorganic matter, dissolved suspended solids, organic nitrogen and specific pollutants (Song et al., 2004). Characterization of tannery industry wastewater considerably changes depending on the size of the industry, the chemical variety and amount used, the amount of water used and the final product (Durai and Rajasimman, 2011).

Various treatment methods such as coagulation-flocculation (Haydar and Aziz, 2009; Mella et al., 2018), biological treatment (El-Sheikh et al., 2011; Balaguer-Arnandis et al., 2017) and advanced treatment processes (Liu et al., 2017; Selvabharathi et al., 2016) are used in the treatment of wastewater of tannery industry. In commonly used chemical treatment methods, the chemicals used bring secondary pollution and intense sludge formation. Conventional biological treatment methods are insufficient in pollutant removal due to the low biodegradability of the tannery industry wastewater.

Electrocoagulation is a common process used for electrochemical treatment. In the electrocoagulation process, suspended, colloidal, or dissolved pollutants in aqueous media can be removed by coagulation, adsorption, absorption, precipitation, and flotation mechanisms (Aygün, 2012). The electrocoagulation process is considered to occur in three consecutive stages:

- Electrolytic oxidation of the electrodes, formation of coagulants,
- Destabilization of pollutants, particle suspension and emulsion breakage,
- Collection of shocks in destabilized phases.
When iron is used as an anode, Fe(OH)\text{n} (n = 2 or 3) forms iron hydroxides in the electrolytic system. The formation of metal hydroxides is shown as two mechanisms in equations (1-8).

1. Mechanism:

Anode:

\[ 4Fe^{2+}_{(k)} \rightarrow 4Fe^{+2}_{(aq)} + 8e^- \]  

\[ 4Fe^{+2}_{(aq)} + 10H_2O_{(l)} + O_2_{(g)} \rightarrow 4Fe(OH)_3_{(k)} + 8H^+ \]  

Cathode:

\[ 8H^+_{(aq)} + 8e^- \rightarrow 4H_2(g) \]  

\[ 4Fe_{(k)} + 10H_2O_{(l)} + O_2_{(g)} \rightarrow 4Fe(OH)_3_{(k)} + 4H_2(g) \]  

2. Mechanism:

Anode:

\[ Fe_{(k)} \rightarrow Fe^{+2}_{(aq)} + 2e^- \]  

\[ Fe^{+2}_{(aq)} \rightarrow 2OH^-_{(aq)} \rightarrow Fe(OH)_{2(k)} \]  

Cathode:

\[ 2H_2O_{(l)} + 2e^- \rightarrow H_2(g) + 2OH^-_{(aq)} \]  

\[ Fe_{(k)} + 2H_2O_{(l)} \rightarrow Fe(OH)_{2(k)} + H_2(g) \]  

2. Materials and Methods

In this study, tannery industry wastewater was used. The wastewater sample was stored at 4 °C and the analyzes were performed according to the Standard Methods recommended (APHA, 2005). The characterization of wastewater is shown in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD, mg/L</td>
<td>3853</td>
</tr>
<tr>
<td>NH\text{3-N}, mg/L</td>
<td>566,2</td>
</tr>
<tr>
<td>TKN, mg/L</td>
<td>833,8</td>
</tr>
<tr>
<td>TSS, mg/L</td>
<td>1465</td>
</tr>
<tr>
<td>TVSS, mg/L</td>
<td>1170</td>
</tr>
<tr>
<td>Chloride, mg/L</td>
<td>21443,5</td>
</tr>
<tr>
<td>pH (20 °C)</td>
<td>3,98</td>
</tr>
<tr>
<td>Conductivity, mS/cm</td>
<td>43,8</td>
</tr>
<tr>
<td>Color, Hazen</td>
<td>700</td>
</tr>
</tbody>
</table>

References


Degradation of the Endocrine Disrupting Micropollutant Bisphenol A with Persulfate - and Peroxymonosulfate-enhanced Ozonation Processes

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Keywords: Endocrine disrupting pollutants, bisphenol A, enhanced ozonation, toxicity, degradation products, experimental design

Abstract

Aqueous bisphenol A (2 mg/L) degradation could be enhanced by persulfate (0.25 mM) and peroxymonosulfate (0.25 mM) - assisted ozonation compared to single ozonation process.

1. Introduction

Recently, a vast number of micropollutants originating from domestic, industrial and agricultural activities have received serious attention because they are threatening the environment and public health. A large number of these emerging contaminants are termed “endocrine disruptors” due to their ability to cause serious malfunction of the endocrine system in several organisms. The extensive use of bisphenol A (BPA) in the plastics and epoxy resins industry has led to increasing reports of its presence in the aquatic environment (as high as 15-20 mg/L in landfill leachate) as well as realization of its potential negative health impacts including cancer, obesity, heart diseases and other body malfunctions. Hence, their effective control and elimination is a major task in water and wastewater management. Until now, various advanced treatment methods including advanced oxidation processes have shown to effectively degrade BPA. Due to increasing operational reliability and cost effectiveness, there is a great potential for the real-scale treatment of BPA with ozone and enhanced ozonation systems (Umur et al., 2013). However, further investigation is urgently needed for a better understanding of the fate of BPA during ozonation as well as the dominant reaction mechanism and aquatic toxicity of BPA’s ozone degradation products.

2. Materials and Methods

Ozonation of 2 mg/L (8.8 µM) aqueous BPA solutions was carried out at a rate of 1.5 L air/min and an ozone feed rate (applied dose) of 7.5 mg/min in the presence of 0.25-0.5 mM persulfate (PS) or peroxymonosulfate (PMS) which were acting as oxidants to enhance the ozonation process. Ozonation and enhanced ozonation conditions were optimized for BPA removal by employing experimental design-response surface methodology (RSM). Evolution of carboxylic acids and changes in acute (Vibrio fischeri) toxicity were also followed during ozonation and enhanced ozonation of BPA samples.

3. Results

BPA degradation could be enhanced by ozonation with 0.25 mM PS, whereas PMS (0.25 - 0.50 mM) had no remarkable effect on BPA removal with ozone. BPA removal was complete at an ozone dose of 30 mg in the presence of 0.25 mM PS; however, 60 mg ozone was required for ozonation with 0.25 mM PMS. For mere ozonation (in the absence of oxidants), an excessive ozone dose (> 60 mg) was needed to achieve complete BPA removal.
As expected, ozone absorption rates increased upon PS addition (from 55% to 60%) due to enhanced ozone decomposition, whereas PMS surprisingly had a slightly “stabilizing effect” on ozone absorption (decreasing from 55% to 50%) rates. Carboxylic acids were followed during ozonation and enhanced ozonation processes. Malonic, muconic and oxalic acid were detected during O3/PS and O3/PMS treatment of BPA (after 1 min ozonation), which completely depleted after 8 min treatment. During mere ozonation, malonic and oxalic acid formation was delayed but quantified after 2 min ozonation, whereas malonic acid disappeared after 6 min mere ozonation. In order to elucidate the dominant reaction mechanism, two different free radical probe chemicals (ethyl alcohol; EtOH and tert-butyl alcohol; TBA) were used at excessive concentrations (44 mM; BPA:probe chemical molar ratio = 1:5000) during ozonation and enhanced ozonation experiments. Results indicated that in the presence of EtOH, BPA removal via ozonation was seriously inhibited (dropping from 92% to 70%), whereas no inhibition was observed in the presence of TBA, indicating that hydroxyl radicals may not be the dominant oxidizing agent. In the case of PS-enhanced ozonation, both alcohols inhibited BPA removals (from 100% to 83% with EtOH and 85% with TBA), whereas in the presence of PMS, the addition of the alcohols did not appreciably retard BPA removals (only by 10% for EtOH; i.e. from 100% to 90%). From the results it could be inferred that the reaction mechanism differed according to the type of ozonation process and particularly hydroxyl radicals were involved in PS-assisted ozonation of BPA (Figure 1). Bioassays were also conducted to examine the toxicity of BPA degradation products during treatment with ozone and PS-assisted ozonation. The acute toxicity towards the marine photobacteria Vibrio fischeri decreased from 22% to practically non-toxic levels (< 5%) after 5 min (ozone dose = 38 mg) ozonation of 2 mg/L BPA in the absence of PS, and from 58% to 12% after 6.5 min (ozone dose = 49 mg) ozonation of 10 mg/L BPA in the presence of 0.5 mM PS.

Figure 1. Degradation of aqueous BPA with ozone (O3), persulfate (PS) and peroxymonosulfate (PMS)-enhanced ozonation processes (PS/O3; PMS/O3) in the absence and presence of the hydroxyl radical (HO) probe chemical tert-butyl alcohol (TBA). Reaction conditions: 2 mg/L BPA; 0.25 mM PS or PMS; 44 mM TBA; applied ozone dose 7.5 mg/min; initial pH 6.5.

References

Leachate Treatment by Electrocoagulation Methods

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Keywords: Electrocoagulation, leachate treatment, COD, Aluminum electrodes, Iron Electrodes

Abstract

In the study, Electrocoagulation (EC) which is known as one of the electrochemical treatment methods was performed for leachate treatment. The study was designed to compare the effectiveness of Aluminum and Iron electrodes reducing the polluting nature of leachate. Batch studies were performed in 500 mL fiberglass reactors with 250 mL leachate sample. Different reaction duration (5, 10, 15, 20 and 25 minutes) and different current values (10, 20, 30, 40, 50 mA/cm²) were performed. The highest efficiency of COD removal from leachate were obtained as 58% The best efficiency for COD, and color removal were achieved at 50 mA/cm² and 25 min. Operating cost for COD, and color removals were calculated as 0.91 USD$/m³ leachate

1. Introduction

A landfill is an engineered method for solid waste disposal and important to protect the environment. In the landfill physical, chemical and biological processes occur. These processes results in the production of gases and leachate [Worrell and Vesilind, 2012]. Leachate has a complex structure and high pollutant load, and its treatment is quite hard to meet the discharge standards. Leachate contains lots of organic or inorganic pollutants with high concentration and measured as BOD, COD, ammonia, heavy metals. Hence, many treatment methods such as biological, chemical, physical, wetland and AOPs, have been performed to treat leachate [İnanç et al., 2000].

In the study was used aluminum electrodes performed EC process. An electrical current is passed through a metal electrode; the anode material undergoes oxidation, while the cathode will be subjected to reduction or reductive deposition of elemental metals. In the case of aluminum, main reactions can be given as [Daneshvar et al., 2006]:

\[ \text{Anode} \quad \text{Al(s)} \rightarrow \text{Al}^{3+} + 3e^- \]

\[ \text{Al}^{3+} \text{ and OH}^- \text{ react with each other to form Al(OH)_3 according to complex precipitation} \]

The main objective of this research was to investigate the optimum operating conditions such as current density (Ampere/m²) and electrolysis time (minute) of leachate by Taguchi method.

The main objective of this research was to investigate the optimum operating conditions such as current density (Ampere/m²) and electrolysis time (minute) of leachate.
2. Materials and Methods

In the study, young-aged leachate with 58 kg COD/m³ was used. Experimental studies were performed in a lab-scale batch mode in a plexiglas reactor. Al electrodes were used both anode and cathode in the study. GW INSTEK GPS 3030 DD was used as DC power supply. The anode and cathode that have the dimensions of 4.5-14 cm, are placed vertically and parallel to each other with inter-electrode distance of 4 cm. The electrodes plates are cleaned manually by washing them in distilled water prior to every run. The volume of effluent taken is 250 mL in electrochemical reactor. The wastewater analyses were done in accordance with The Standard Methods for Examination of Water and Wastewater [APHA, 1998].

3. Results

COD and color results are expressed as percentage of removal (%) through the following equation:

\[
\text{Removal efficiency (\%) =} \frac{\text{Ci} - \text{Ce}}{\text{Ci}} \times 100
\]

Where; C\text{ is the initial concentration and C\text{ is the final concentration of the pollutant (mg/L and ptc).}

According to obtained results, the order of importance of the parameters affecting the EC process were determined as pH > current density > reaction time for the COD removal efficiency, and pH > reaction time > current density for the dissolved COD and color removal efficiency.

References


Adsorption of Ketoprofen onto powdered activated carbon: Effect of adsorbent dose and solution temperature

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Keywords: Ketoprofen, NSAID, powder activated carbon.

Abstract

This work investigates the adsorption of Ketoprofen, an NSAID (non-steroidal anti-inflammatory drug) onto a powder activated carbon. The effect of Ketoprofen dose, equilibrium time and temperature of solution on the equilibrium adsorption capacity is investigated through batch tests. The experimental results show that the adsorption capacity of Ketoprofen decreases from 18.40 to 0.26mg/g with the increase of the adsorbent mass of 0.05 to 4g respectively. The optimal mass of the adsorbent that gives the maximum Ketoprofen elimination is equal to 0.25g. The equilibrium time was very fast estimated by 5min for all the masses studied, which indicates the rapidity of the adsorption process and that the activated carbon is a very good adsorbent of Ketoprofen. The temperature of solution has partially no effect on the amount adsorbed of Ketoprofen, the optimal temperature of 25°C gives a very high percentage of elimination of Ketoprofen.

1. Introduction

Environmental water pollution has a big concerns, the quality of wastewater from industrial or domestic sources requires effective treatment and has complied with the standards submitted by states to preserve the environment. The major problem that makes treatment difficult is the variety of water contaminants, which can have various sources.

Drug substances are among the most toxic pollutants of water, the presence of these in the water even at low concentrations can cause serious problem. Pharmaceuticals are products, relating to the protection and promotion of health, the pharmaceutical products include the drug, biological reagents, pharmacy chemicals, galenic products, dressing objects and all other products necessary for the human and veterinary medicine, from these products the drugs are defined [1]

"Medicinal product" means any substance or composition presented as possessing curative or preventive properties with regard to human or animal diseases, all products that may be administered to humans or animals for the purpose of establishing a medical diagnosis or to restore, correct, modify their organic functions [1]. Among the different drugs manufactured and sold, we find anti-inflammatories:

An anti-inflammatory is a medicine to fight inflammation. It is a group of drugs intended to treat an inflammatory reaction and the resulting diseases such as rheumatic manifestations, fractures, stomatitis and genital and urinary lesions.

Many anti-inflammatories are over-the-counter. Like all drugs, they can cause side effects and can cause poisoning, including overdose or interaction with other drugs, as well as
allergies. Anti-inflammatory drugs include steroids (glucocorticoids or steroidal anti-inflammatory drugs) and non-steroidal anti-inflammatory drugs [1].

This drug can be found in the effluents of the pharmaceutical industry at more or less significant concentrations. With this in mind, Ketoprofen was chosen as a water pollutant in this work while exposing their processes of elimination. The technique of elimination proposed is the adsorption in batch system as its simple design and not expensive process.

2. Materials and Methods

2.1. Adsorbent

In this work a commercial powdered activated carbon PAC (Biochem Chemopharma) was used as adsorbent. The PAC has an average diameter less than or equal to 63μm, it was chosen as adsorbent because of its efficiency to adsorb different molecules. Before use the PAC was dried at a temperature of 105° C to remove the adsorbed water.

The PAC was characterized by measuring the pH\textsubscript{PZC} value and acidic/basic surface functional groups. The experimental protocol used for the measure of isoelectric point is that described by Nandi et al [2]. The technique consist to prepare solutions of NaCl at 0.01M at different initial pHs ranging from 2 to 12, the pH was adjusted by addition of HCl and/or NaOH at 0.1M. A volume of 50mL of each solution was been contacts with (0.1g) masses of activated carbon with stirring for 48h. The pH\textsubscript{PZC} is determined by the value for which the pH\textsubscript{final} is equal to the initial pH. (The pH\textsubscript{PZC} is the point where the pH\textsubscript{final} = pH\textsubscript{initial} curve intercepts the pH\textsubscript{final} = Initial pH line). The results obtained are shown in Figure II.1. The results obtained show that the pH\textsubscript{pzc} value determinate by the intersection of the two curves (final pH = initial pH), is equal to 7.1.

The acidic and basic surface functional groups were determinate by the Bohem titration method [3]. The results obtained (Table.1) show that the number of acidic functional groups is greater than that of the basic ones. The hydroxyl and phenol groups are predominant followed by the strong carboxylic acid groups, while the lactone and weak carboxylic acid groups are zero.

<table>
<thead>
<tr>
<th>Concentration of Functional Groups</th>
<th>meq.g\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong carboxylic acid (G I)</td>
<td>0.16</td>
</tr>
<tr>
<td>Lactone and weak carboxylic acid (G II)</td>
<td>0</td>
</tr>
<tr>
<td>Hydroxyl and Phenol (G III)</td>
<td>0.55</td>
</tr>
<tr>
<td>Acidic Functional Groups</td>
<td>0.71</td>
</tr>
<tr>
<td>Basic Functional Groups</td>
<td>0</td>
</tr>
</tbody>
</table>

2.2. Adsorbate
Ketoprofen used in this study was purchased from BEC Chemicals. Ketoprofen is the racemic (RS) -2- (3-benzoylphenyl) propionic acid. The R enantiomer is called dexketoprofen and a drug of the family of nonsteroidal anti-inflammatory drugs (NSAIDs) [4]. Ketoprofen-based drugs have analgesic effects. The best known is the Ketum. Figure 1 shows the chemical structure of Ketoprofen. The main proprieties of Ketoprofen are summarized in Table 2. All Other chemicals used for the experiments were analytical grads.

![Chemical structure of Ketoprofen](image)

**Figure 1.** Chemical structure of Ketoprofen: R-ketoprofen (a) and S-ketoprofen (b) [5].

**Table 2.** Physico-chemical characteristics and composition of Ketoprofen [4, 5]

<table>
<thead>
<tr>
<th>UICPA Name</th>
<th>2-(3-benzyolphenyl) propionic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>White crystalline powder</td>
</tr>
<tr>
<td>The molecular formula</td>
<td>C_{16}H_{14}O_{3} [isomer]</td>
</tr>
<tr>
<td>Molar mass</td>
<td>254.2806± 0.0147 g mol^{-1}</td>
</tr>
<tr>
<td></td>
<td>C : 75.57%, H : 5.55%, O : 18.88%</td>
</tr>
<tr>
<td>T° fusion</td>
<td>94°C</td>
</tr>
<tr>
<td>Solubility</td>
<td>51 mg.L^{-1} at 22°C</td>
</tr>
<tr>
<td>pKa</td>
<td>4, 54 at 25 °C</td>
</tr>
<tr>
<td>λ_{max} (measurable value)</td>
<td>254 nm</td>
</tr>
<tr>
<td>Heavy metals</td>
<td>10 ppm</td>
</tr>
<tr>
<td>Loss on drying</td>
<td>0.25%</td>
</tr>
<tr>
<td>Dosage of C_{16}H_{14}O_{3}</td>
<td>100%</td>
</tr>
<tr>
<td>Residual solvent</td>
<td>Benzene, toluene</td>
</tr>
</tbody>
</table>

2.3. Preparation of adsorbate solution
A stock solution was prepared by dissolving 50 mg of Ketoprofen in the form of powder in 1L of distilled water. The suspension is stirred for 24 hours until the complete dissolution of the Ketoprofen. Successive dilutions were used to obtain working solutions of the desired concentrations.

2.4. Batch reactor adsorption test

Ketoprofen adsorption tests using activated carbon are carried out in batch mode at a temperature of 25±1°C in a 400 mL beaker. Thus, a mass of 0.1 g of activated carbon is brought into contact with 100 mL of an aqueous solution of Ketoprofen at a concentration of 10 mg/L. The temperature is kept constant using a water bath (Kottermann Labortechnik) and stirring is ensured by means of a heating plate and agitation (Agimatic-N) and is kept constant at 300 rpm.

Sample at a volume of 2.5 mL was taken out from the beaker at a specified time interval until the adsorption equilibrium was reached and filtered using Millipore filters (0.22 μm). The recovered filtrate is immediately analyzed by spectrophotometer (Shimadzu mini 1601) and is returned to the batch reactor to maintain the volume of the solution to be treated constant.

The amount adsorbed is determined from the following equation [6]:

\[ q_e = \frac{(C_0 - C_t)V}{m} \]

Were:

- \( C_0 \): the initial concentration of Ketoprofen [mg.L\(^{-1}\)]
- \( C_t \): the concentration of Ketoprofen at time t [mg.L\(^{-1}\)]
- V: Volume of the solution [L]
- m: Dose of the adsorbent [g]
- \( q_e \): The amount adsorbed at time t

The present study was conducted using varying adsorbent dose, contact time and solution temperature.

3. Results

3.1. Effect of adsorbent dose and contact time

To examine the influence of the adsorbent dose on the Ketoprofen adsorption, the mass of activated carbon was varied from 0.05 to 4 g and the other parameters are kept constant. The results obtained are shown in Figure.2.a and Figure.2.b
The results (Figure 2.a) show that the adsorption capacity of Ketoprofen decreases from 18.40 to 0.26 mg/g with the increase of the adsorbent dose from 0.05 to 4 g respectively. In addition, the percentage of elimination increases from 92.8 to 97.89%. This is justified by the greater availability of the adsorbent surface area and consequently the number of active sites.

We noted also from Figure 2.b that the optimal mass of the adsorbent that gives the maximum Ketoprofen elimination is equal to 0.5 g. But, as there is not much difference...
between two values of percentage of elimination obtained (97.72 ≈ 97.89%) for the two dose adsorbent of 0.25 and 0.5 g, the mass of 0.25 g was chosen as optimal mass in our work.

The equilibrium time was very fast estimated by 5 min for all the masses studied, which indicates the speed of the adsorption process and that the activated carbon is a very good adsorbent of Ketoprofen.

3.2. The effect of temperature

This parameter is important for the establishment of kinetic adsorption models, for which we have studied the variation of the adsorbed quantity as a function of time at different temperatures (20, 25, 30, 40, 50°C), the results obtained are shown in Figure 3.

The amount of Ketoprofen adsorbed is practically the same for all the studied temperatures (≈ 94%) with the exception of the temperature of 25°C, at this temperature we observe a slight increase of the amount adsorbed of Ketoprofen (3.79 mg·g⁻¹). Overall, the percentage removal decreases from 97.02 to 94.51% with increasing temperature from 25 to 50°C respectively. This can be explained by the exothermicity of the adsorption process and the weakening of the bonds between Ketoprofen and adsorbent active sites for the highest temperatures [7].

The ambient temperature of 25°C gives a very high percentage of elimination of Ketoprofen, so this value is considered as an optimal value.

4. Conclusion

Our objective in this chapter is to study the effects of the few operating parameters, such as adsorbent mass, equilibrium time and solution temperature on the adsorption of Ketoprofen by activated carbon. The results obtained show that the adsorption capacity of Ketoprofen per unit mass decreases from 18.40 to 0.26 mg·g⁻¹ when the mass increases from 0.05 to 4 g.
respectively, the optimal mass which gives the maximum of Ketoprofen elimination is equal to 0.25g. The equilibrium time was very fast estimated by 5min for all the masses studied, which indicates the speed of the adsorption. The temperature of the optimal solution is 25°C, this value gives the largest amount adsorbed Ketoprofen (3.79mg.g⁻¹).

References


High Performance Adsorption Capability of Geopolymer Prepared from Tin Tailing Minerals

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Keywords: Tailing waste, Adsorption, Dye Adsorption

Abstract

Tin tailing is one of the tin mining wastes, and it is environmentally desirable. This research is aimed to utilize tin tailing to be useful for other environmental problems; dye containing waste water treatment, via adsorption. The adsorbent was prepared by geopolymer formation using sodium silicate and soybean oil as modifier. Physicochemical study of the adsorbent was conducted by x-ray diffraction (XRD), gas sorption analyzer and scanning electron microscope-energy dispersive x-ray (SEM-EDX). Furthermore, adsorption capability of the geopolymer was evaluated in a batch adsorption of methyl violet solution. The results showed that prepared geopolymer demonstrated superior adsorption capability for methyl violet. The adsorption capability is depend on the temperature of adsorption system. Furthermore, kinetics study on the adsorption process is discussed.

1. Introduction

Mining waste is one of the potential problem source from mining industries, instead of some advantages from them. Tailing is a kind of problem regarding to some possible toxic effect of metal waste in it. In other aspect, tailing solid contains clay and clay minerals having capability to be modified for more functional application such as adsorption purposes. This properties meets with the other environmental problem such as dye waste contamination from home scale of batiks industrial activity in Indonesia. Synthesis of adsorbent from tailing waste was proposed by modifying the minerals to form a geopolymer. Physicochemical characteristics of material was studied by some instrumental analyses such as scanning electron microscope, x-ray diffraction and gas sorption analysis. Adsorption capability of the material was evaluated in a batch adsorption system toward rhodamine B solution. Kinetics and mechanisms was studied by using spectrophotometric analysis and applied into some kinetics and adsorption isotherm models. The kinetics study indicated the excellent adsorption capability of the geopolymer was discussed in this paper.

2. Materials and Methods

Materials: Tailing waste was obtained from PT. Timah mining area, Belitung, Sumatra island, soybean oil was purchased from PT. Indofood sukses makmur (Indonesia), tetra ethyl ortho silicate and methyl violet (MV) were purchased from Merck-Millipore (Germany).

Material Preparation: Geopolymer was prepared by mixing the tailing minerals, soybean oil and TEOS in a certain portion. The mixture was dried in an oven before calcination.
Physicochemical study of the adsorbent was conducted by x-ray diffraction (XRD), gas sorption analyzer and scanning electron microscope-energy dispersive x-ray (SEM-EDX). Furthermore, adsorption capability of the geopolymer was evaluated in a batch adsorption of methyl violet solution in varied MV concentration.

3. Results

![Figure 1. XRD pattern of raw material and geopolymer](image)

![Figure 2. Intraparticle diffusion model of MV adsorption using prepared geopolymer](image)

From the physicochemical characteristics data, it is obtained that the tailing mineral consists of dominantly mullite mineral, and there is no significant change after modification into geopolymer (Yugeswaran et al., 2010). The geopolymer exhibits capability to adsorb MW and the kinetics of the adsorption fit to the intraparticle diffusion model (Wu et al., 2009).

References


Physicochemical and Photocatalytic Studies of ZnO-supported Indonesian Kaolinite (ZnO/Kaolinite) for Methyl Violet Photo-oxidation

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Keywords: ZnO, Photocatalyst, Kaolinite, Dye degradation

Abstract

Research on preparation of photocatalyst of ZnO-supported onto Indonesian Kaolinite (ZnO/Kaolinite) and photocatalytic activity for methyl violet photo-oxidation has been conducted. ZnO/Kaolinite was prepared by impregnation method utilizing zinc acetate as ZnO precursor and kaolinite sample obtained from Bangka Belitung province, Indonesia. Physicochemical study of the photocatalyst was conducted by x-ray diffraction (XRD), gas sorption analyzer and scanning electrone microscope-energy dispersive x-ray (SEM-EDX). Furthermore, photocatalytic activity of the material was evaluated in a batch photo-oxidation system of methyl violet degradation. The results showed that prepared ZnO/Kaolinite demonstrated superior and high stable photocatalytic performance in the photooxidation system. The prepared ZnO/Kaolinite is a simply prepared, recovered and reused for advanced application of dye wastewater treatment.

1. Introduction

Photocatalysis is one of popular techniques for dye-containing wastewater treatment. Many photocatalysts were applied for certain dye degradation, and in order to enhance photocatalyst activity and its reusability, immobilization of photocatalytic active material in a solid support (Lathasree et al., 2004) (Fatimah and Sopia, 2017). In this research, immobilization of ZnO in a clay material: kaolinite was conducted. Physicochemical characterization of prepared photocatalyst was performed by using x-ray diffraction (XRD), gas sorption analyzer (GSA), scanning electron microscope-energy dispersive x-ray (SEM-EDX), and the photocatalytic activity was tested in methyl violet photodegradation.

2. Materials and Methods

Materials: Kaolinite was obtained from Sukabumi, West Java, methyl violet was purchased from PT. from Merck-Millipore (Germany). Material Preparation: ZnO/Kaolinite was prepared by dispersing zinc acetate in kaolinite solid followed by calcination. Physicochemical study of the adsorbent was conducted by x-ray diffraction (XRD), gas sorption analyzer and scanning electron microscope-energy dispersive x-ray (SEM-EDX). Furthermore, photocatalytic activity of the photocatalyst was evaluated in a batch reactor of methyl violet degradation. The kinetics of photocatalytic degradation was evaluated by spectrophotometric analysis of treated solution.
3. Results

![Figure 1. UV-Vis spectra of treated solution](image1.png)

XRD pattern shows the attached ZnO as shown by reflections at at $2\theta = 31.67^\circ$, $34.31^\circ$, $36.14^\circ$, $47.40^\circ$, $56.52^\circ$, $62.73^\circ$, $66.28^\circ$, $67.91^\circ$, $69.03^\circ$, and $72.48^\circ$ (Akhtar et al., 2012). The photocatalytic degradation mechanism was revealed by the reduction of MV spectra along increasing time of treatment and the shift of maximum wavelength at lower region as indication of methylation of the MV.

**References**


Preparation of Activated Carbon from Waste Tire and Its Use for Dye Remove

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Keywords: Waste tires, methylene blue, adsorption, activation, activated carbon, pyrolysis

Abstract

In the first phase of this study, thermochemical processes were used to investigate the attainability of active carbon from tires that have completed their lifetime. In active carbon production stage, the granulated waste tires were first washed in KOH solution at 1:1 (1-K) and 1:2 (2-K) impregnation ratios prior to thermal activation. Chemically activated waste tires were then subjected to pyrolysis. After pyrolysis, solids (char) were used as active carbon. The surface area of the 2-K adsorbent was measured to be 2.945 m²/g by BET analysis. In the second stage of the study, adsorption removal of methylene blue dye from synthetically prepared wastewater was investigated using 1-K and 2-K active carbons produced. It was investigated that the active carbon produced in the study can be used as an appropriate adsorbent for the removal of the colorant with the adsorption process. Isotherm, kinetic and thermodynamic studies were carried out in order to better understand the adsorption mechanisms for active carbons. At the end of the thermochemical and adsorption studies carried out, it is considered that the study is applicable to large scale because active carbon obtained from the tire which has completed its lifetime is close to commercial active carbon properties and that it provided good efficiency in adsorption on the dye and that it is an alternative method of recovery of waste tires.

1. Introduction

Approximately 17 million tonnes of waste rubber are produced every year worldwide, and this figure is constantly increasing (Onay and Koca, 2015). Waste tires can be evaluated as national wealth and storage in solid waste disposal areas is against the legislation. Storing waste tires in solid waste disposal areas without evaluation is costly, as well as causing many health and environmental problems (Life Longer Completion Control Regulation, 2006, Saleh et al., 2014). Spreading use areas of the lacquer materials and giving buyer centering cause various environmental problems in the ecosystem. Methods for removal of stain materials from aqueous solutions and reverse osmosis, ion exchange, adsorption, etc. are used. The methods used in wastewater treatment are reverse osmosis, ion exchange, electrodialysis and electrolysis (Yagub et al., 2014). However, some methods have limitations such as low efficiency, sensitive applications, and high cost. The adsorption process is one of the most effective and efficient methods that can be applied in the removal of the excipient when a suitable adsorbent is used and is widely used (Pezoti et al., 2014; Özbaş et al., 2013). In this study, the effect of adsorbent amount, dye concentration, contact time, pH and temperature on the removal of synthetic Methylene Blue (MM) paint by activated carbon adsorption from waste tires was investigated. At the hands of activated carbon; chemical and thermal activation methods have been used. Adsorption experiments were carried out in a continuous adsorption system.
2. Materials and Methods

In the first stage of active carbon production, the granulated waste tires were first washed in KOH solution at 1:1 and 1:2 impregnation ratios prior to thermal activation. The two different impregnated waste tires obtained were then subjected to pyrolysis. Pyrolysis was carried out at 700 °C for 2 hours. The reactor was supplied in an inert, oxygen-free environment in the reactor by feeding nitrogen gas (N₂) with a flow rate of 1 L/min. Among the liquid-solid-gas products containing high energy obtained after thermal treatment, solids (char) were used as active carbon. The obtained activated carbon were investigated by SEM (Scan Electron Microscope Analysis), BET (surface area measurement), elemental analysis and thermal value analysis. In adsorption stage of this study, the effect of adsorbent amount, pH, temperature and contact time on adsorption process was investigated.

3. Results

The effect of adsorbent amount, pH, temperature and contact time on adsorption process was investigated. For 2-K adsorbent in which optimum yield was obtained pH was 6.5, temperature was 30 °C, adsorbed dose was 7.5 gr/L, contact time was 30 minutes. Under these conditions, 83% dye removal yield was obtained.

Adsorption studies with 2-K adsorbent showed compatibility with Freundlich and Temkin isotherms; kinetic studies showed a pseudo second order kinetic model. The Gibbs free energy change (ΔG°) at the end of the thermodynamic studies for 10, 20, 30, 40 °C temperatures were -30.88, -32.19, -33.54, -31.21 kJ/mole, respectively. Adsorption enthalpy (ΔH°) was found to be -7.017 kJ/mole, and adsorption entropy (ΔS°) was found to be 0.0853 kJ/mole.K. It was determined that the adsorption system is an exothermic and spontaneous process.

Table 1. BET analysis results for 1-K and 2-K adsorbents.

<table>
<thead>
<tr>
<th>Material</th>
<th>1-K Adsorbents (m²/g)</th>
<th>2-K Adsorbents (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>After chemical activation</td>
<td>2.867</td>
<td>2.945</td>
</tr>
<tr>
<td>After chemical+thermal activation</td>
<td>36.268</td>
<td>42.61</td>
</tr>
<tr>
<td>Waste tire</td>
<td>1.349</td>
<td></td>
</tr>
</tbody>
</table>

References

Regulations on Control of End-of-Life Tires, (25.10.2006 and 26357 Number ) (in Turkish).
Degradation of Olive Pomace by Thermochemical Methods

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Keywords: Gasification, pyrolysis, pomace, recycle, energy

Abstract

The elimination of waste from the globalized world is reducing the tolerance of nature. This is why developed world countries are working on energy recovery from wastes. The use of wastes with high organic content as fuel instead of fossil fuels to generate energy is necessary for the sustainability of the environment. Pomace is a solid waste resulting from the production of olive oil. As a result of the analysis, it was determined that raw pomace contained 46.33% carbon, 1.26% nitrogen and 5.42% hydrogen. As a result, the calorific value of the raw pomace was measured as 4659 cal/g. In this study, raw pomace was converted to a product of higher calorific value by pyrolysis. Carbon-enriched pomace was subjected to gasification process with appropriate dry air gas flow. Effective syngases, CH₄, H₂ and CO, were obtained for recovery after gasification. When the findings obtained in this study are examined; the pyrolysis and gasification method can be used as an alternative method in terms of evaluable product retention in the management of the pomace, which creates serious environmental problems in our country and in certain regions of the world.

1. Introduction

During the production of olive oil, pomace, which is formed as a solid by-product, poses serious problems. Pomace is still widely used as a fuel in residential areas in industrial environments (Güneysu, 2003). Pyrolysis is an alternative to classical combustion and is a thermochemical destruction process that involves the conversion of wastes into smaller molecules and flammable gases in an inert gas atmosphere instead of oxygen. The process consists of methane, complex hydrocarbons, flammable gases such as hydrogen and carbon monoxide, liquids and solids (Zhao et al., 2010). Gasification is the physical and chemical degradation of organic constituents by heat under a poor oxygen environment. The resulting products are char, ash, slag and syngas. The main components of the syngas are carbon monoxide (CO), hydrogen (H₂), methane (CH₄), carbon dioxide (CO₂), ethane (C₂H₆), water (H₂O) and nitrogen (N₂). Syngas has thermal value and can be used as an energy source by re-burning (Higman and Burgt, 2007).

2. Materials and Methods

In this study, the pomace produced in the olive oil production facility in İncirliova District of Aydın Province was used. The plant produces olive oil continuously. Elemental analysis of the raw rice samples used in the study and of the solid products (biochar) obtained as a result of the experiments were made. In the elemental analysis experiments, the quantities C, H, N and S of the samples determined. ABB brand AO2020 model continuous gas analyzer, located in Department of Environmental Engineering, Department of Istanbul University, was used for synthetic gas measurements.
3. Results

![Figure 1. Pyrolysis at 500 °C, 1L/min N₂ + Gasification at 750 °C, 0.05L/min dry air](image)

The synthesis gas with the highest calorific value has 16% H₂ and 15% CH₄ gases (Figure 1). These gases can be burned as a closed system at the outlet and used in the energy field or can be supplied to the atmosphere by burning in the conventional manner. During the production of olive oil, pomace, which is formed as waste, can be used as raw material for fuel for energy recovery. It has been observed that the pyrolysis pretreatment gasification experiment at 500°C produces high calorific value solid product and syngas.

References


Change in the Available and Toxic Concentrations of Metals in the Soil When Compost and Commercial Soil Conditioners are Used

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bIstanbul University, Institute of Graduate Studies in Science and Engineering, Vezneciler, Istanbul, Turkey.

Keywords: Soil remediation, metal, soil conditioners

Abstract

Heavy metals are among natural components of soil. Most heavy metals, except for iron, exist in soil in low concentrations (generally in lower amounts than 100 mg/kg dry soil; iron can be found in concentrations above 5000 mg/kg). Some heavy metals like trace elements (for instance: copper, selenium, zinc) are required to sustain metabolism of human body. However, they can be toxic in high concentrations. In addition, heavy metals are dangerous because they tend to bio-accumulate. Compost is used as organic conditioner in agriculture as it contains high amounts of nutrient and stable organic substances. It is also used for the treatment of polluted soils and water. In this study, it is aimed to examine the changes in the immediately available, potentially available and toxic concentrations of metals found in the acidic character soil when using municipal solid waste compost (MSW), lime (CaCO3) and commercial soil conditioners (A2 and T50). When the TCLP test results are examined, it is seen that the concentrations that can be regarded as the amount of compost added to the soil increases as toxic concentrations for heavy metals decrease.

1. Introduction

It has been proven that heavy metals are toxic effects of biological accumulation in plants and animals. For this reason, it is very important to implement remediation techniques on areas contaminated with heavy metals (Tunah, 2015). It is possible to treat soils contaminated with metals by various methods such as phytoremediation, soil washing, stabilization, solidification, electroremediation and excavation (Mulligan et al., 2001; Kumpiene et al., 2008). Organic materials of diverse origins such as municipal solid waste, food industry waste and composts from animal fertilizers can be used to cure contaminated soils from heavy metals (Clemente et al., 2007; Nwachukwu and Pulford, 2008). The addition of organic substances to contaminated soils has positive or negative effects on the mobility of metals depending on the properties of the material and receiving soil (eg soil pH, organic matter and clay content) (Farrell and Jones, 2010). Soil lime addition is one of the most common remediation methods and can lead to the settling of heavy metals as metal-carbonates and considerably reduces the exchangeable parts of heavy metals in the soil (Lee et al., 2004).

2. Materials and Methods

In this study, 10% (v/v) compost, 25% (v/v) compost, 50% (v/v) compost, 1.5% (v/v) lime, 2.5% (v/v) lime, 1.5% lime and 10% compost, 1.5% (v/v) A2, 2.5% (v/v) A2, 5% (v/v) A2, 2.5% (v/v) A2 and 10% (v/v) compost, 0.5% (v/v) T50, 1.5 % (v/v) T50, 2.5% (v/v) T50, 1.5% (v/v) T50 and 10% (v/v) compost were added in soil. Municipal solid waste compost is provided from ISTAÇ Kemerburgaz Recovery and Compost Facility. A2 and T50 commercial soil conditioners were obtained from the international company.
Virotec. Determination of mobility and forms of heavy metals in the soil before and after remediation by applying Elemental Analysis to soil, compost and prepared pots soil. Immediately Available Element Concentration Determination Method, Potentially Available Element Concentration Determination Method and TCLP (toxicity characteristic leaching procedure) Method were applied. Only irrigation was applied to the pot for one week in order to allow time for the substances added to the soil to react with the soil. At the end of the week, seeds of maize (*Zea mays saccharata*) were planted, one for each pot. Plant seeds are planted in the pot where the soil is not made any addition. The prepared pots were placed under automatic timer-controlled lighting, which was set to expose to daylight, 16 hours a day, 8 hours a night. In the pot experiments, the development of the maize seeds (*Zea mays saccharata*) in the mixture of the soil and the healers was observed for 40 days.

3. Results

**Table 1. Results of TCLP test**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample Number</th>
<th>Zn</th>
<th>Pb</th>
<th>Cd</th>
<th>Ni</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td>1</td>
<td>1043.25</td>
<td>5.61</td>
<td>2.98</td>
<td>0.23</td>
<td>275.88</td>
<td>227.43</td>
<td>3.26</td>
</tr>
<tr>
<td>Soil + 10% (v/v) compost</td>
<td>2</td>
<td>599.75</td>
<td>9.76</td>
<td>2.02</td>
<td>0.1</td>
<td>106.95</td>
<td>14.06</td>
<td>4.53</td>
</tr>
<tr>
<td>Soil + 25% (v/v) compost</td>
<td>3</td>
<td>583.55</td>
<td>2.02</td>
<td>0.9</td>
<td>0.08</td>
<td>19.58</td>
<td>2.77</td>
<td>11.37</td>
</tr>
<tr>
<td>Soil + 50% (v/v) compost</td>
<td>4</td>
<td>32.17</td>
<td>3.73</td>
<td>N.D.</td>
<td>0.02</td>
<td>9.79</td>
<td>39.6</td>
<td>5.17</td>
</tr>
<tr>
<td>Soil + 1.5% (v/v) Lime</td>
<td>5</td>
<td>14.52</td>
<td>2.28</td>
<td>0.21</td>
<td>0.54</td>
<td>1.53</td>
<td>5.48</td>
<td>0.29</td>
</tr>
<tr>
<td>Soil + 2.5% (v/v) Lime</td>
<td>6</td>
<td>7.36</td>
<td>0.54</td>
<td>N.D.</td>
<td>N.D.</td>
<td>1.58</td>
<td>0.15</td>
<td>0.11</td>
</tr>
<tr>
<td>Soil + 1.5% (v/v) Lime + 10% (v/v) compost</td>
<td>7</td>
<td>16.26</td>
<td>7.5</td>
<td>0.11</td>
<td>N.D.</td>
<td>7.46</td>
<td>31.91</td>
<td>0.55</td>
</tr>
<tr>
<td>Soil + 1.5% (v/v) A2</td>
<td>8</td>
<td>611.23</td>
<td>8.46</td>
<td>1.9</td>
<td>N.D.</td>
<td>138.95</td>
<td>5.19</td>
<td>2.37</td>
</tr>
<tr>
<td>Soil + 2.5% (v/v) A2</td>
<td>9</td>
<td>425.8</td>
<td>9.2</td>
<td>1.2</td>
<td>N.D.</td>
<td>77.48</td>
<td>7.41</td>
<td>1.76</td>
</tr>
<tr>
<td>Soil + 5% (v/v) A2</td>
<td>10</td>
<td>519.75</td>
<td>5.71</td>
<td>1.12</td>
<td>0.29</td>
<td>4.27</td>
<td>15.57</td>
<td>1.9</td>
</tr>
<tr>
<td>Soil + 2.5% (v/v) A2 + 10% (v/v) compost</td>
<td>11</td>
<td>1269.75</td>
<td>13.02</td>
<td>2.46</td>
<td>0.21</td>
<td>48.77</td>
<td>26.28</td>
<td>8.19</td>
</tr>
<tr>
<td>Soil + 0.5% (v/v) T50</td>
<td>12</td>
<td>1314.75</td>
<td>16.72</td>
<td>3.8</td>
<td>1.05</td>
<td>162.23</td>
<td>24.45</td>
<td>4.02</td>
</tr>
<tr>
<td>Soil + 1.5% (v/v) T50</td>
<td>13</td>
<td>118.43</td>
<td>1.06</td>
<td>0.21</td>
<td>N.D.</td>
<td>4.2</td>
<td>0.47</td>
<td>1.75</td>
</tr>
<tr>
<td>Soil + 2.5% (v/v) T50</td>
<td>14</td>
<td>21.38</td>
<td>0.86</td>
<td>0.23</td>
<td>0.49</td>
<td>4.04</td>
<td>1.99</td>
<td>0.54</td>
</tr>
<tr>
<td>Soil + 1.5% (v/v) T50 + 10% (v/v) compost</td>
<td>15</td>
<td>8.29</td>
<td>1.4</td>
<td>0.02</td>
<td>129.18</td>
<td>2.3</td>
<td>24.45</td>
<td>69.26</td>
</tr>
</tbody>
</table>

**References**


Abstract

Today, the number of wastewater treatment plants is rapidly increasing. Accordingly, there is a large increase in the amount of sewage sludge. The sewage sludge obtained should be disposed of in such a way as not to damage the environment. Among these methods, disposal of sewage sludge by landfill is one of the most suitable methods in terms of environment and economics. In this study, the wastewater treatment sludge from the beer industry treatment plant and the solid product obtained from the pyrolysis result of this sludge were used. Growth of “Allium Ascalonicum” was observed in soil samples improved with these materials and in soil samples enriched with artificial fertilizer addition. As a result, it can be seen that the materials used can be used for remediation of the soil and contribute to the development of the plant.

1. Introduction

The background and nature of issue or problem. Sewage sludge is a type of solid waste containing 0.25-12% solids by weight, depending on the treatment applied, which is odorous, semi-solid in the liquid formed as a result of wastewater treatment. The micro and micro nutrients in the sludge that emerged as a result of the treatment are a beneficial fertilizer to this waste; and organic substances provide a good soil improvement feature, many authorities support the use of these products in agriculture and applications are spreading in many countries (Strauch,D.,1991,Düring ve Gäth,2002). Within the framework of the European Union Directives; composting, biometanization and landmass application with energy recovery and recovery methods to reduce the storage of biodegradable waste in landfills. It is also appropriate to use treatment sludge not only for agriculture but also for green space, land recreation and urban landscape (Debosz et al., 2002). Nowadays it is a very common practice to supply the treatment sludges having suitable properties to agricultural areas and to use them. Both the final disposal and the plant nutrients in the sludge become natural cycles of the soil (Kocaer et al., 2003) by applying the treatment sludges to the soil in accordance with the agriculture. Waste incineration / gasification (thermal conversion) is the process of converting combustible waste to an inert residue (ash, slag) at high temperatures. By means of the method, while the space required for the storage of solid wastes is reduced, energy recovery is achieved by using the heat that is present in the waste and which is produced as a result of the treatment (Öztürk,2016). Pyrolysis is a process based on thermal decomposition of waste in a completely oxygen-free environment. With the pyrolysis method, coke, tar, volatile oils, condensable hydrocarbons, water and pyrolysis gases are released as a result of disposal of wastes. In the gasification method, a
certain amount of air is given but the amount of oxygen in the environment is kept below the stoichiometric ratio (Saltabaş et al., 2009)

2. Materials and Methods

In this study, Tropical brand 100% organic plant land was purchased. Compost which is recycled from the domestic solid waste obtained from Istan Kemerburgaz Recovery and Compost Facility in mixture prepared with plant fertilizer, ammonium sulphate containing 21% Nitrogen obtained from Gübretaş as artificial fertilizer, high purification sludge containing organic matter content from beer factory and pyrolysis of this brewery sludge the resultant brewery waste water was mixed at the ratios indicated in Table 3 and placed in a pot. The flower pots were added with 1 shallow onions and the soil was moistened with water. The pots were monitored for a total of 24 hours, with 8 hours of night time and 16 hours of daylight. This study was carried out in Istanbul University Faculty of Engineering Laboratory.

3. Results

<table>
<thead>
<tr>
<th>Soil mixtures</th>
<th>pH at the end of study</th>
<th>Root length (cm)</th>
<th>Body length (cm)</th>
<th>Weight (gr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td>6</td>
<td>9</td>
<td>25.75</td>
<td>1.6</td>
</tr>
<tr>
<td>Soil + 50%(v/v) Compost</td>
<td>7.5</td>
<td>11.75</td>
<td>18.5</td>
<td>1.23</td>
</tr>
<tr>
<td>Soil + 25% (v/v) Compost</td>
<td>7</td>
<td>12.15</td>
<td>29.9</td>
<td>2.4</td>
</tr>
<tr>
<td>Soil + 2.5% (v/v) fertilizer</td>
<td>5</td>
<td>1</td>
<td>13.85</td>
<td>0.7</td>
</tr>
<tr>
<td>Soil + 1.5% (v/v) fertilizer</td>
<td>5</td>
<td>5.85</td>
<td>27.75</td>
<td>2.038</td>
</tr>
<tr>
<td>Soil + 25% (v/v) Brewery sludge</td>
<td>5.5</td>
<td>2.5</td>
<td>31</td>
<td>3.5</td>
</tr>
<tr>
<td>Soil + 10% (v/v) Brewery sludge</td>
<td>6.5</td>
<td>7</td>
<td>28.25</td>
<td>2.75</td>
</tr>
<tr>
<td>Soil + 10% (v/v) solid product of brewery sludge pyrolysis + 25% (v/v) compost</td>
<td>7</td>
<td>9.5</td>
<td>2.09</td>
<td>1.5</td>
</tr>
<tr>
<td>Soil + 10% (v/v) solid product of brewery sludge pyrolysis</td>
<td>5.5</td>
<td>17</td>
<td>36.5</td>
<td>2.829</td>
</tr>
</tbody>
</table>

As a result, in this study, the most useful matter for plant growth was found to be the solid product obtained from pyrolysis of brewery sludge.

References


The Effects of Thermal Prosses Solid Product on Development of Cicar Arietinum L.

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Keywords: waste water treatment sludge, pyrolysis, plant growth, zero waste

Abstract

In the study, the effects on the development of *Cicer Arietinum* plant were investigated by adding municipal solid waste compost, brewery sludge, pyrolysis solid product of brewery sludge and artificial fertilizer at certain rates to the soil in order to improve the soil and increase the yield. The change in the size of the plant (body and root), weight of the plant were examined. The research was carried out at 20-25 °C temperatures, 16 hours at day and 8 hours at night in the laboratory environments of Istanbul University Engineering Faculty.

As a result of the study, it was observed that the soil mixture obtained by mixing the pyrolysis solid product with soil at certain ratios positively affected plant growth. Soil and pyrolysis solid product (25%) provided the highest yield.

1. Introduction

The background and nature of issue or problem. Biochar produced by carbonization of biomass with pyrolysis are used for soil remediation and as a plant fertilizer to store carbon in the soil, increase soil fertility, reduce climate change (reduce CO₂ and CH₄ emissions), dispose of waste causing environmental pollution in waste management and generate energy (Akgul, 2017). Within the framework of the European Union Directives; composting, biometanization and landmass application with energy recovery and recovery methods to reduce the storage of biodegradable waste in landfills. It is also appropriate to use treatment sludge not only for agriculture but also for green space, land recreation and urban landscape (Debosz et al., 2002). Many studies have shown that the application of treatment sludge and compost in appropriate quantities improves the physical properties of soil and plant growth (Hanay and Hasar, 2007). Pyrolysis is the process of burning biomass under limited oxygen or at high temperatures without oxygen (300-700°C). Products of this process; solid phases (biochar), gas (syngas) containing H₂, CH₄, CO, CO₂ and other gases, tar and liquid (bio-oil) containing various oils and coal granule, carbon and other inert materials (Saltabaş et al., 2009).

The aim of this study is to investigate the effects of biochar on plant growth (*Cicer Arietinum L.*), obtained from the pyrolysis of the sludge plant sludge.

2. Materials and Methods

As organic improver, domestic solid waste compost (obtained from İSTĄÇ compost plant), artificial fertilizer, treatment sludge (from a brewery waste water treatment plant) and heat treatment solid product (pyrolysis product of brewery sludge) were used. As a plant material, natural field crop chickpeas grown in summer in Tokat province were used.
At 20-25 °C temperature, artificial lighting connected to automatic timer 16 hours daylight, 8 hours night lighting was done.

3. Results

Table 1. Plant height, root length, weight and pH measurements at the end of the study

<table>
<thead>
<tr>
<th>Soil mixture</th>
<th>Body height (cm)</th>
<th>Root length (cm)</th>
<th>Weight (gr)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td>19</td>
<td>9</td>
<td>0.11</td>
<td>6</td>
</tr>
<tr>
<td>Soil +25%(v/v) brewery sludge</td>
<td>16.25</td>
<td>5.85</td>
<td>0.3</td>
<td>5.5</td>
</tr>
<tr>
<td>Soil+10% (v/v)brewery sludge</td>
<td>19.75</td>
<td>9</td>
<td>0.64</td>
<td>5</td>
</tr>
<tr>
<td>Soil + 25% (v/v) biochar</td>
<td>25.5</td>
<td>11</td>
<td>1.0595</td>
<td>7</td>
</tr>
<tr>
<td>Soil +10% (v/v) biochar</td>
<td>23.5</td>
<td>13.25</td>
<td>1.07</td>
<td>7</td>
</tr>
<tr>
<td>Soil+ 50% (v/v) compost</td>
<td>13.5</td>
<td>6.5</td>
<td>0.92</td>
<td>7.5</td>
</tr>
<tr>
<td>Soil+ 25% (v/v) compost</td>
<td>19.25</td>
<td>5.5</td>
<td>0.88</td>
<td>7</td>
</tr>
<tr>
<td>Soil+2.5%(v/v) artificial fertilizer</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>Soil +1.5%(v/v) artificial fertilizer</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>5.5</td>
</tr>
<tr>
<td>Soil+ 10% (v/v) biochar+25% (v/v) compost</td>
<td>21</td>
<td>9</td>
<td>0.95</td>
<td>7</td>
</tr>
</tbody>
</table>

In this study, which is the main theme of 'zero waste', it was determined that the waste sludge from the wastewater treatment plant should be evaluated in this area and it could be used as an efficiency refiner and soil conditioner in agriculture sector. Thus, the problem of disposal of the treatment sludge, which is called waste, can be overcome and the treatment sludge can provide income to operate.

References

Recycling of Wastewater from Petroleum Refinery

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Keywords: Petroleum refinery, Waste water, Recycling

Abstract
Rapid industrial development and urbanization have resulted in social, political and economic problems in many countries. Forests, freshwater resources, seas, and the vital resources for living are adversely affected by industrialization and urbanization. Environmental problems arise as a consequence of the pollution of these resources, which are necessary for human life, from industrial activities. The rapid progress of these activities means the end of resource use. For this reason, the crude oil in the petroleum industry is subjected to certain operations after refinery arrives. The wastes and wastewaters that form in the units as well as the wastes are formed. These are treated in the refinery. Recycling systems are used to reuse wastewater from the treatment plant. In this study, information on the recovery of wastewater from oil refineries was given.

1. Introduction
The crude oil extracted from underground is converted to petroleum products after passing through certain stages and is called refinery (URL1). Crude oil is a mixture. Crude oil is a mixture of gas, liquid and solid hydrocarbons and their isomers (URL2). As a result of refining and processing of crude oil in refineries, the average of 43% gasoline, 18% fuel oil, 11% LPG (liquefied petroleum gas, propane or propane-butane mixture), 9% jet fuel, 5% asphalt and 14% other products is obtained (URL3). Wastewater from petroleum refinery; (a) Process wastewater: Wastewater generated by contamination of water used in processes in petroleum processing units as a result of processes at certain stages or during processing, (b) Non-Process Wastewater: It is the wastes that separate from the operations in the petroleum refinery, (c) Domestic Wastewater: These wastes can be counted as waste arising from the needs of people working in the refinery environment (URL4).

2. Materials and Methods
Waste water treatment in petroleum refineries is carried out as follows;
Physical Treatment: In oil refineries, wastewater to the treatment plant comes from the tank area, oily waste water and rain water through the channel line. Closed systems come from ballast systems. The overall system is fed from the oily wastewater system. Oily wastewater from the system first passes through the grid. The waste water passing through the grills comes to the separator system. The separator is a separator used to separate oil, fuel and other liquid components in oily waste water. There is a scraper system in the separator. With the help of the strippers in the seperator, the oil on the water surface is separated. Separated oil is sent to slop tanks and used again in crude oil processing plants. The remainder passes through the spaces in the system to the balancing pool. Physical treatment ends after reaching the balancing pool. Chemical Treatment: The chemical treatment begins with the
equilibrium pool and ends with coagulation, flocculation, and dissolved air flotation (DAF). Wastewater treatment comes to the point of discharge from physical, chemical and biological treatments. When some of the wastewater is discharged to the sea at the discharge point, the determined part is drawn with the help of pumps. Thus, wastewater recovery starts. In advance treatment, mechanical filters, sand filters, activated carbon, ultra filtration and reverse osmosis are used in petroleum refineries.

3. Results

Improper treatment of industrial wastewater or wastes causes contamination of fresh water resources and degradation of quality. For this reason, industrial wastewater and wastes must be treated. Industrial wastewater needs to be refined at the level that will provide the specified standards in order to keep the living quality of the living unchanged and leave a better world for future generations. To conserve natural resources, each industry must invest in the necessary systems to recover their wastewater.

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URL4. https://xzenon34.files.wordpress.com/2012/03/6-cakmakci_ipek_ozkaya_ders_notu.pdf
Reuse of Waste Water for Agricultural Irrigation

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Keywords: Waste water, recycling, reuse, agriculture, irrigation

Abstract

Recycling of wastewater is important. Because, the quality of the water is gradually decreasing. This makes reuse of wastewater important as well. Increasing pollution of underground and surface waters and reduction of water quality make recycling and reuse of wastewater attractive. It is known that the prevention of water shortage, one of the most sensitive issues in the life cycle, is a possible and effective solution to the recovery and reuse of waste water. It is possible to reduce the amount of water used for urban, industrial, agricultural and industrial purposes by recycling and reusing wastewater. Within the scope of this study, the recovery of wastewater and reuse for irrigation in agriculture are discussed.

1. Introduction

Another definition of water that is important for reuse of recycled water is water shortage. Water scarcity; is defined as the amount of water per capita. According to the Falkenmark Water Intake Index (the amount of water a cubic meter per capita per year). It has been determined that there is a water richness of 1700m$^3$ and above, the presence of 1700m$^3$ - 1000m$^3$ water stress, 1000m$^3$ - 500m$^3$ water shortage and absolute water shortage when less than 500m$^3$. Countries with average annual water per capita below 1000m$^3$ per year are defined as water-poor (Kurtkulak, 2014). The amount of water per capita in Turkey 1519m$^3$. Turkey is a candidate to become one of the water-poor countries in 2030 with 1168m$^3$ (TÜİK, 2018). Waste water recovery and reuse provide an effective way to solve problems in terms of periodic droughts. The water will be regenerated as water reclamation protects the natural life cycle and new fresh water resources are not reduced. The World Health Organization (WHO) refers to worldwide reuse of wastewater as: recognition of water pollution, wastewater and source value of gray waters, water scarcity and stress, food safety issues with increasing population and pollution, environmental waste from inappropriate wastewater disposal (Pintilie et al., 2016).

2. Materials and Methods

Depending on many factors such as the choice of method of application for the recovery of wastewater and the intended use of the recycled water, the characteristics of the site being applied, the shape of the land, the state of the water resources, the socio-economic characteristics of the users. At the same time, local government planning, wastewater reclamation policies and legal regulations are also important. For this reason, there are serious application differences in terms of wastewater recovery, even among countries and even states (EPA, 2010).
3. Results

As water demand and environmental needs increase, water recycling will play a greater role in the overall water resource. With water recycling and water conservation, vital water resources can be managed in a sustainable way. Purified wastewater is most commonly used in agricultural irrigation. By means of agricultural irrigation, both the nutrients in the wastewater provide fertilizer demand for the soil and it is beneficial by being economical with the disposal of wastewater. However, if adequate treatment is not provided, the use of this water will be detrimental because of the pathogens, helminths, bacteria and viruses it contains but the negativities caused by the controls can be reduced. The most important danger of reused waters is the diseases that can be transmitted by microorganisms. The quality of irrigation waters varies depending on where they are used, irrigation water can be lower in pasture and straw farming.

References

EPA 2012, Global Water Intelligence - Urban Wastewater Recovery Market Report
Investigation of Energy Recovery from Waste Paper Cups

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Keywords: Waste paper cups, Gasification, Syngas

Abstract

In this study, the production of syngas and valuable product recovery from waste paper cups were investigated by using gasification process. The gasification experiments were carried out in a dry-air-entrained fixed bed cyclone separator reactor. This work has revealed that the gasification process can be achieved in valuable liquid and solid products as compared to burning with the recovery of these type of waste.

1. Introduction

As a consequence of modern life, the need for energy increases day by day for private and also industrial use. Fossil fuels used as energy sources constitute a global problem on the environment and and all living creatures. For this reason, the use of energy from renewable energy sources and from fuels derived from waste has an increasing interest in recent years. Paper cups that entered our daily life with the spread of disposable products, are consumed abundantly by many people in the world and are formed huge amount of waste. In spite of the high amount of cellulose content of the paper cup, the dissolution of them in nature constitute a problem due to the polymer bonds and other additives in the paper, therefore the final disposal must be provided by applying appropriate methods.

The recycle of waste paper cups can not be applied together with other paper waste due to their physicochemical structures. Since, different compounds can be used in production of paper cups depending on the brand and purpose of use. The paper cups contains cellulose, polyethylene (PE), silicone oils, and silicone adhesives in their composition by varying amounts. This limits the recycling options and leads to be classified them as a problematic waste (Mitchell et al., 2013).

2. Materials and Methods

In this study, obtaining solid, liquid and gaseous products from waste paper cups has been investigated by using gasification process. A batch cyclone separator gasification reactor was used in the experiments. 0.005 L/min dry air was used as the agent gas. The gasification experiments were carried out at 500, 600, 700 and 725°C. Moisture, ash and solids content, elemental analysis and calorific value tests were carried out to determine physical and chemical properties of waste paper cups. The ratio of solid, liquid and gas products and the calorific value of syngas were examined at the end of each experimental runs.

3. Results

Syngas rich in CH₄ and H₂ gases was obtained in the gasification experiments carried out with fixed dry air entrainment flow rate of 0.05 L/min and at different temperatures (500, 600, 700, 725°C). When the calorific values of the obtained syngas were examined, it was
determined that the calorific values were changed between 2036 kcal/kg and 3137 kcal/kg. The highest calorific values were reached in the gasification test carried out at 700 °C. The differences on the amounts of solid, liquid and gaseous products obtained in experimental studies are presented in Table 1.

Table 1. The amounts of solid, liquid and gas products obtained from gasification experiments

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Gasification condition</th>
<th>Raw material (g)</th>
<th>Liquid Products (g)</th>
<th>Solid products (g)</th>
<th>Syngas (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>Dried air-0.05 L/min; 500 °C</td>
<td>50</td>
<td>8.76</td>
<td>8.08</td>
<td>33.16</td>
</tr>
<tr>
<td>G2</td>
<td>Dried air-0.05 L/min; 600 °C</td>
<td>50</td>
<td>13.07</td>
<td>7.46</td>
<td>29.47</td>
</tr>
<tr>
<td>G3</td>
<td>Dried air-0.05 L/min; 700 °C</td>
<td>50</td>
<td>10.17</td>
<td>8.37</td>
<td>31.46</td>
</tr>
<tr>
<td>G4</td>
<td>Dried air-0.05 L/min; 725 °C</td>
<td>50</td>
<td>7.95</td>
<td>6.25</td>
<td>35.8</td>
</tr>
</tbody>
</table>

The composition of the syngas for the experiment at the temperature of 700 °C in which the highest calorific value is reached, is presented in Figure 1.

Figure 1. The syngas composition during the gasification at 700 °C – 0.05 L/min dry air

References

Photo Fenton-like Degradation of Methylene Blue with Cobalt Ferrite Nanoparticles

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Keywords: cobalt ferrite nanoparticles, Fenton-like, heterogeneous catalyst, methylene blue, photo degradation

Abstract

In this work, the synthesis and characterization of cobalt ferrite nanoparticles (CoFe₂O₄ NPs) were carried out. The characterization studies confirmed that the synthesized particles were determined to be CoFe₂O₄ NPs in nanoscale and cubic spinel structure. The photo Fenton-like degradation ability of CoFe₂O₄ NPs was also evaluated and the results demonstrated that the synergistic effect of combining of Co and Fe₂O₄ enabled CoFe₂O₄ NPs become the promising photo Fenton-like catalyst for degradation of MB from aqueous solutions. At the optimum experimental conditions (3.0 of initial pH, 25 mM of H₂O₂ concentration, 50 mg/L of initial dye concentration, and 1.0 g/L of catalyst concentration), nearly 100% decolourisation efficiency was achieved after the photo Fenton-like degradation of MB in the presence of CoFe₂O₄ NPs heterogeneous catalyst with near-UV radiation.

1. Introduction

Nowadays, dyes are used in almost all production sectors in industry; therefore dye-laden wastewaters pollute natural waters and lower their value in use. In recent years, advanced oxidation processes (AOPs) such as Fenton and photo-Fenton processes, ozonation, electrochemical oxidation, photolysis with H₂O₂ and O₃ electro-Fenton, which are based on the production and the oxidative action of hydroxyl radicals, have attracted great attention for the treatment of a wide range of organic pollutants in wastewaters. The photo Fenton-like (UV/H₂O₂) process could be used promptly as a hopeful and attractive treatment method for an effective decolorization and degradation of dyes in a textile wastewater. Recently, the using spinel ferrite (MFe₂O₄) magnetic nanocomposites as heterogeneous catalyst especially in wastewater treatment applications, has gained much attention owing to their distinctive magnetic assets and chemical stability. Moreover, it is easy to remove spinel ferrites magnetic nanocomposites from the treated waste by applying external magnetic material and recycled. Cobalt ferrite (CoFe₂O₄) magnetic nanoparticles are indispensable metal oxide and they have exclusive applications in various fields like sensor, semiconductor photocatalysts, biomedical etc. It is n-type semiconductor, highly stable, small optical band gaps (2.0 eV) making them active under visible light treatment [1]. In the present study, cobalt ferrite (CoFe₂O₄) magnetic nanoparticles were synthesized, characterized, and used as heterogeneous catalyst to investigate the possibility of decolourisation of Methylene Blue (MB) dye by photo Fenton-like process.

2. Materials and Methods

The synthesis of cobalt ferrite nanoparticles: CoFe₂O₄ nanoparticles have been synthesized by chemical precipitation method. The essential mass of ferric nitrate (Fe(NO₃)₃.6H₂O) and cobalt nitrate (Co(NO₃)₂.4H₂O) was taken in a stoichiometric ratio of 2:1 and dissolved in distilled water. Then, 1M of NaOH aqueous solution was added as a reductant to adjust the
pH 10, then the formed solution was kept at an ambient temperature of 80 °C for 3 hours to obtain a thick precipitate. The obtained product was centrifuged using double distilled water and then dried in a hot air oven at 80 °C for 24 h. The dried product was powdered well by a mortar and calcinated at 500 °C for 3 h in a furnace as the result CoFe2O4 nanoparticles were obtained and characterized [2].

**Photo Fenton-like Degradation Experiments:** Photo Fenton-like activity of CoFe2O4 nanoparticles was examined by evaluating the degradation of organic Methylene blue (MB) dye in the presence of aqueous solution under irradiation of visible light with a high pressure mercury lamp (165 W). In the photo Fenton-like experiments, 0.05 g of CoFe2O4NPs, except for catalyst concentration experiments, was added to solutions containing 50 mL of MB solution at known initial pH and initial dye concentrations. Prior to irradiating, the flasks containing the solutions were agitated in the water bath in dark for 20 minutes to make certain desorption-adsorption equilibrium of MB aqueous solution with the nanocatalyst. Then the aqueous solution with the catalyst was exposed to light after addition of 5 ml of H2O2 solutions. The samples were taken at pre-determined time intervals and they were centrifuged to remove ferrite nanoparticles. The concentration of MB was observed with the UV-vis spectrophotometer at the wavelength of 665 nm. The decolourisation percentage for MB was expressed in terms of the decrease in UV-vis absorbance.

3. Results

Cobalt ferrite nanoparticles (CoFe2O4 NPs) were synthesized by chemical co-precipitation and the results of characterization studies were presented below:

- According to XRD pattern; the synthesized nanoparticles have characteristic peaks of cubic spinel phase. SEM images showed that the synthesized particles were in nanoscales and porous structures.

The synthesized CoFe2O4 NPs were evaluated as heterogeneous photo Fenton-like catalyst in the degradation of MB. The degradation was achieved in presence of near-UV light when both oxidant (H2O2) and catalyst were present together in the reaction medium, thus proving that the dye was decolorized by photo Fenton-like reaction. The obtained results were given below:

- The effects of initial pH, H2O2 concentration, initial dye concentration, and catalyst concentration on the photo Fenton-like reaction were investigated. The optimum initial pH, H2O2 concentration, and catalyst concentration were determined to be 3.0, 25 mM, and 1.0 g/L, respectively. At these optimum conditions, almost 100% decolourisation efficiency was obtained. Besides, the photo Fenton-like activity of Fe2O4 nanoparticles was also investigated and it was found that Fe2O4 nanoparticles did not have photo Fenton-like activity for MB degradation. So, it can be concluded that the addition of Co to the ferrite (Fe2O4) nanoparticles provide having the photo Fenton-like activity of the nanoparticles.

Consequently, the present study have revealed significant outputs to synthesis of an effective photo Fenton-like heterogeneous catalyst, which could be important for the contribution to the related literature as well as the water treatment applications.

References


Colorimetric Detection of Fe$^{3+}$ Ions in Aqueous Solution Using Green-Synthesized Silver Nanoparticles

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Keywords: Bauhinia variegata leaf extract, colorimetric sensor, detection of Fe$^{3+}$ ions, green synthesis, silver nanoparticles

Abstract

In this study, the green synthesis and characterization of silver nanoparticles (AgNPs) from orchid tree (Bauhinia variegata) leaf extract was firstly carried out and then the usability of AgNPs as a colorimetric sensor for detection of Fe$^{3+}$ ions in aqueous solutions was evaluated. The characterization studies showed that the synthesized particles were determined to be AgNPs in nanoscale and face-centered cubic structure. Besides, the total phenolic content of B. variegata extract was determined to be 1.826±2.1 mg gallic acid equivalents/g dry leaf. Also, the green-synthesized AgNPs showed a strong surface plasmon resonance (SPR) around 430 nm and $\lambda_{\text{SPR}}$ intensity decreased with the increasing of Fe$^{3+}$ concentration in aqueous solution. Based on the linear relationship between the change of $\lambda_{\text{SPR}}$ intensity and Fe$^{3+}$ ion concentration, AgNPs can be used for the sensitive and selective detection of Fe$^{3+}$ ions in aqueous solutions with a linear range of 6-100 μM and a detection limit of 2.08×10$^{-6}$ M.

1. Introduction

There are various analytical techniques such as atomic absorption spectrometry, inductively coupled plasma mass spectrometry, and inductively coupled plasma emission spectrometry for the detection of metal ions. However, these methods usually require sophisticated equipments, technical expertise, and tedious sample preparation steps. Therefore; it is thought that these techniques are not economical and user-friendly. Recently, the colorimetric detection technique has been widely used to detect metal ions in aqueous solutions as it is cost-effective and requires less time. Nowadays, metallic nanoparticles can be widely used for colorimetric detection of metal ions due to their strong surface plasmon resonance (SPR), stable dispersion, bio-compatibility, and controllable physical/chemical properties. Among the metallic nanoparticles; it is well-known that silver nanoparticles (AgNPs) have the strongest SPR; for this reason, most of SPR-related fundamental investigations and sensing applications have focused on AgNPs [1]. For these works, it is important to study with environmentally-friendly and low-cost nanoparticle-based sensor; in this regard, the green synthesis method is frequently preferred for the synthesis of metallic nanoparticles. So; in this study, AgNPs were synthesized with a green, simple, one-pot, low-cost, and stabilizer-free method for the detection of Fe$^{3+}$ ions in aqueous solutions.

2. Materials and Methods

Green Synthesis and Characterization of AgNPs: Orchid tree (Bauhinia variegata) leaves were collected from Çiftlikköy Campus of Mersin University and then 5 g of the purified and dried leaves were boiled in 600 mL of distilled water. As-prepared aqueous leaf extract was used a reducing agent in the green synthesis of AgNPs. For this purpose, 5.0 mL of the aqueous leaf extract was added to 100 mL of 10$^{-3}$ M AgNO$_3$ solution. Then, the mixture
was stirred magnetically at room temperature for 1 h. After that, the resulting mixture was centrifuged and the precipitated AgNPs were washed with distilled water and dried at 110 °C in an oven for 24 h. Finally 0.015 g of the dried AgNPs were dispersed in 100 mL of distilled water for the colorimetric detection studies. The dried AgNPs were used for characterization studies such as XRD, zetasizer using DLS technique, and FTIR [2].

Colorimetric Detection: The colorimetric detection studies of the different species such as Na+, K+, Mg2+, Ba2+, Ni2+, Mn2+, Cu2+, Zn2+, Fe3+, and Cd2+ with AgNPs were carried out by a series of experiments. 1 ml of 100 mM metal ion solution (for example Fe 3+) was added to the mixture containing 2 mL of 0.15 g/L AgNPs solution and 1 mL of the distilled water. Approximately 5 minutes later, the absorbance value of the prepared solution was recorded at 430 nm by UV-vis spectrophotometer and their spectra were scanned at a wavelength range of 300-700 nm. Experimental and analysis methods were repeated for the other metal ions. The maximum increasing in the SPR of AgNPs and disappearance of color was observed only in the presence of Fe3+. Thus, different concentrations of Fe3+ (1-100 μM) were used to determine the linear detectable range and limit of detection by means of decreasing in the λ_{SPR} intensity of AgNPs [1].

3. Results

The results of the green synthesis, characterization and the colorimetric detection for the metal ions of silver nanoparticles (AgNPs) from orchid tree (Bauhinia variegata) leaf extract were given in below:

- It was observed from FT-IR spectrum that AgNPs contained the functional groups of many phenolic substances resulting from leaf extract. The typical powder XRD pattern showed that AgNPs had face-centered cubic structure. According to DLS analysis, the average hydraulic diameter of AgNPs was found to be 22.07 nm.
- The total phenolic content of B. variegata extract was determined to be 1.826±2.1 mg gallic acid equivalents/g dry leaf by Folin-Ciocalteu colorimetric method adapted from Slinkard and Singleton (1977). Thus, the obtained FTIR peaks and the calculated phenolic content confirmed that the phenolic substances in the aqueous leaf extract played important roles in the reduction of Ag1+ (AgNO3) into Ag0 (AgNPs).
- It was determined in the investigation of the selectivity of AgNPs that only AgNPs solution containing Fe3+ ions had the color change from brown to colorless. Besides, the λ_{SPR} of AgNPs solution containing Fe3+ ions disappeared whilst any significant change in the λ_{SPR} intensity was not obtained for AgNPs solutions containing the other metal ions.
- The investigation of the sensitivity of AgNPs indicated that the λ_{SPR} and color intensities of AgNPs solutions containing Fe3+ ions at different concentrations decreased gradually with the increase in Fe3+ ion concentration. Moreover, limit of detection (LOD=3σ/s) for Fe3+ ions of AgNPs colorimetric sensor was determined to be 2.08×10^{-6} M, which is relatively lower compared to the related literature [3, 4].

Consequently, the results showed that the green-synthesized AgNPs can be used as an effective colorimetric sensor for detection of Fe3+ ions in aqueous solution.

References

Removal of Reactive Black 5 With Fenton Oxidation From Aqueous Solutions And Optimization of Response Surface Methodology

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Keywords: Color Removal, Fenton Processes, Optimization, Reactive Black 5

Abstract

In this study, color removal from anionic Reactive Black 5 (RB5) dye solutions with fenton oxidation process was investigated. The experimental design and optimization of color removal performance by using Response Surface Methodology (RSM) were studied. pH, dye concentration, Fe$^{2+}$ dose and H$_2$O$_2$ dose parameters selected for independent variables to RSM and determined designs were performed. The fenton oxidation experiments were carried out that initial solution pH (2.5-5.5), dye solution concentration (50-350 mg/L), Fe$^{2+}$ dose (25-55 mg/L), H$_2$O$_2$ dose (175-425 mg/L), and constant temperature (30°C).

The decreasing pH and concentration increased the color removal capacity of the reactants. The color removal performance increased with increasing reactant amounts. According to experiment results color removal of RB5 dye efficiencies obtained over 99%. Conditions that was obtained maximum removal efficiencies for RB5 respectively are; pH 2.5, dye concentration 120 ppm, Fe$^{2+}$ 25 ppm and H$_2$O$_2$ dose 240 ppm. Full quadratic models were predicted for the response variable and final values of response were in good agreement with calculated values, thus R$^2$ value confirming the reliability of resulting model equation is 96.2%.

1. Introduction

Textile products are used in various fields in our daily life. Because of the differences in production, dyed wastewater is produced in large quantities and containing different types of pollutants [1]. More than 4000 years of dyeing materials are used for textile dyeing [2]. The volume of dyestuffs that discharging to receiving water is very high and poses a danger to this environment. When these wastewater is discharged, it affects the environment aesthetically, aquatic atmosphere obstructs light and oxygen input, and causes negative results on the ecosystem [3]. Due to the toxicity content, the living things in the receiving environment have a negative effect [4]. Color removal in painted waste water; is difficult due to the low biodegradability of the dye material [5]. For this reason, color removal in wastewater requires the use of mechanical, chemical and advanced treatment techniques instead of conventional treatment methods [6]. In our study, color removal was investigated by fenton oxidation, which is a advanced treatment technique.

2. Materials and Methods

Experimental studies have been carried out on synthetic dye solutions that commonly used in the textile industry. Fenton oxidation experiments were carried out in a 1 L temperature controlled jacketed reactor.
The color of the aqueous dye solutions were measured by colorimetric method. The maximum wavelength of the RB5 was determined of 597 nm. Color removal efficiency was calculated by the following equation;

\[
\% \text{ Color Removal Efficiency} = \frac{C_0 - C_s}{C_0} \times 100
\]  

(1)

Where, \(C_0\) and \(C_s\) are the concentration of an outward solution and its initial concentration (ppm).

3. Results

It is seen that as the pH and the initial concentration of the dye material increase, the recovery efficiency is adversely affected. With an increase of \(Fe^{+2}\), the yield increases to a certain point. The increase in \(H_2O_2\) increases the efficiency in the presence of the appropriate iron ion.

Table 1. Optimum conditions for RB5 color removal

<table>
<thead>
<tr>
<th>High (1,000)</th>
<th>Low (50)</th>
<th>pH (2.50)</th>
<th>(Fe^{+2}) (25)</th>
<th>(H_2O_2) (175)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>360.0</td>
<td>5.0</td>
<td>55.0</td>
<td>325.0</td>
</tr>
<tr>
<td>Maximum Giderim</td>
<td>102,1574</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composite Desirability</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Giderim Maximum (y = 102,1574)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d = 1,000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

References

D-optimal Design Study of Reactive Extraction of Propionic Acid with Imidazolium-Based Ionic Liquids

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Keywords: Propionic acid, Ionic liquids, Reactive extraction, Response surface methodology, D-optimal design.

Abstract

In this design work, reactive extraction of propionic acid from aqueous solutions by using imidazolium-based ionic liquids was examined. Hydrophobic ionic liquids, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [BMIM][Tf₂N], 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF₆], were used as diluents. Tributyl phosphate (TBP) as an extractant in ionic liquids was used. D-optimal design based on the response surface methodology (RSM) has been applied to determine the effect of different variables on reactive extraction process. Initial propionic acid concentration, extractant (TBP) concentration, temperature were chosen as numerical variables and type of ionic liquid was chosen as a categorical variable. Extraction efficiency, selected as a dependent variable, was calculated from the experimental data. The model equation for the extraction efficiency was acquired to explain characteristics of reactive extraction process for the removal of propionic acid.

1. Introduction

Propionic acid has large using in different chemical applications and industries. Especially it is widely used in production of cellulose plastics, ester solvents, perfume bases, arthritis drugs, herbicides, and plasticizers. Also, it is used to suppress the growth of mold and rope in breads and cakes in food industry and it is used as mold preventives in hay and silage [1]. Propionic acid is generally obtained by the fermentation process and is acquired not only as a single product but as by-product with aqueous solutions. The by-product formation is a major problem that reduces the production efficiency. It must be removed from the fermentation broths for the continuous fermentation process [2-3].

2. Materials and Methods

Acid solutions were prepared by dissolution of a known quantity of propionic acid in distilled water. Organic solutions were prepared by dissolving of TBP in imidazolium-based ionic liquids. The volumes of acid and organic solutions were 2 mL. Experiments were performed by shaking in a water bath at 150 rpm for 1 h. Then, the samples were centrifuged in 3000 rpm for 10 min to separate the phases. The propionic acid concentration in the aqueous phase was determined by titration with NaOH solution of 0.1 N. The concentration of propionic acid in the organic phase was calculated from the material balance.

3. Results

D-optimal design based on the response surface methodology (RSM) has been applied to determine the effect of different variables on reactive extraction process. For the purpose, Design-Expert® Software Version 11 Trial, (Stat-Ease, Inc., Minneapolis, USA) was used.
The design variables (numerical and categorical variables) and their levels were chosen as given in Table 1. These factors and their levels were entered into Design-Expert® Software, 24 experiments were obtained and these experiments were carried out.

**Table 1.** Design variables and their levels used in D-optimal design.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Code</th>
<th>Categorical</th>
<th>Code</th>
<th>Numerical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial acid concentration (%)</td>
<td>(X_1)</td>
<td>Numerical</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>TBP concentration (mol/L)</td>
<td>(X_2)</td>
<td>Numerical</td>
<td>0</td>
<td>1.5</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>(X_3)</td>
<td>Numerical</td>
<td>25</td>
<td>35</td>
</tr>
<tr>
<td>Ionic liquid type</td>
<td>(X_4)</td>
<td>Categorical</td>
<td>[BMIM][PF6]</td>
<td>[BMIM][Tf2N]</td>
</tr>
</tbody>
</table>

Three-dimensional (3D) response surface plots were illustrated to determine the relationship between the numerical variables and extraction efficiency. Figure 1 shows the effect of numerical variables on the extraction efficiency.

**Figure 1.** Response surface plots for the effect of initial acid concentration, TBP concentration and temperature on extraction efficiency at the center levels. (Ionic liquid type: [BMIM][PF6])

**References**

Separation of Valeric Acid from Aqueous Solutions by Reactive Extraction using 1-Hexyl-3-methylimidazolium hexafluorophosphate

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Keywords: Valeric acid, Reactive extraction, Ionic liquid, Tributyl phosphate.

Abstract

The objective of this work is to investigate separation of valeric acid from aqueous solutions by reactive extraction using ionic liquid. As hydrophobic ionic liquid, 1-Hexyl-3-methylimidazolium hexafluorophosphate, [HMIM][PF₆], was used. As a reagent in ionic liquid, tributyl phosphate (TBP) was used. The effect of different parameters on separation such as initial valeric acid concentration, reagent (TBP) concentration and temperature was investigated. Extraction efficiencies (E), distribution coefficients (D) and loading factors (Z) were calculated from the experimental results. This reactive extraction study by using TBP dissolved in ionic liquid [HMIM][PF₆] showed that it was an effective technique for the separation of valeric acid from aqueous solutions.

1. Introduction

Valeric acid, pentanoic acid or short chain straight fatty acid, is extensively used in variety of industrial applications such as lubricants, plasticizers, biodegradable solvents, perfumes, flavors, and pharmaceuticals. It is also used as monomer in polymerization processes. It is a subproduct in the production of adipic acid, and it must be separated during the purification of adipic acid [1-2]. Organophosphorous compounds, such as tributyl phosphate (TBP), have been widely used as reagents for the removal and recovery of carboxylic acids from aqueous solutions, such as wastewaters and fermentation broths [2]. Reactive extraction of carboxylic acids from aqueous solutions including lower than 10% (w/w) acid concentrations, has been provides a higher separation efficiency. The conventional organic solvents used in extraction cause environmental pollution because they have toxic, flammable and volatile properties. Recently, ionic liquids are considered as alternative solvents to replace conventional organic solvents [3]. In view of this, separation of valeric acid from aqueous solutions by reactive extraction using ionic liquid [HMIM][PF₆] and TBP was investigated in this study.

2. Materials and Methods

Valeric acid solutions were prepared with distilled water. Organic solutions were prepared by dissolution of TBP in ionic liquid [HMIM][PF₆]. 2 mL of acid and organic solutions were added to glass flasks and shaken for optimum time in a water bath with a vibrating rate of 150 rpm. And then, they were centrifuged in 3000 rpm for 10 min to separate two phases. The concentrations of acid in the aqueous phases were measured by the automatic titrator (SI Analytics, Schott Titroline) by using 0.1 N NaOH. The concentrations of acid in the organic phases were also determined by means of the mass balance.
3. Results

The effect of equilibrium time on reactive extraction of valeric acid was shown in Figure 1. As can be seen from Figure 1, the equilibrium time for reactive extraction of valeric acid was determined as 60 min.

![Figure 1. The effect of equilibrium time on reactive extraction of valeric acid.](image)

References


Abstract

The aim of investigation is to recover of lactic acid from water by Amberlite IRA-400. Adsorption time, the initial concentration of lactic acid, the amount of Amberlite IRA-400 and temperature have been selected as the parameters affecting on adsorption. The adsorption capacities of Amberlite IRA-400 under various conditions were detected and compared with each other. It has been determined that significant amount of lactic acid was recovered by Amberlite IRA-400. Langmuir, Freundlich and Temkin isotherms were used to explain the adsorption mechanism. Kinetic models such as Pseudo-first order, Pseudo-second order kinetic models were used and also Weber-Morris intra-particle diffusion model was applied. Among the isotherms used, Freundlich was found as the best fit the experimental results for lactic acid adsorption with value of $R^2=0.9935$. Besides, the most favorable model was determined as Pseudo-second order kinetic model ($R^2=0.9972$).

1. Introduction

Lactic acid is known as an alpha-hydroxy acid. It contains carboxylic and hydroxyl groups. These groups play significant roles in various chemical production processes. Lactic acid has been used as a raw material for the production of polylactic acid which is a biodegradable polymer. Furthermore, lactic acid has also been used in the production of many chemicals such as acrylic acid, propionic acid, pyruvic acid, propylene glycol, acetaldehyde and 2,3-pentanedione. It has been also used in different industries such as food, cosmetic, pharmaceutical and textile industries. Lactic acid can be obtained by either biological or chemical synthesis. However, it is widely produced in aqueous solutions by fermentation processes. Also, it occurs in wastewaters and effluents in many industrial facilities [1]. Thus, it is very significant to recover lactic acid from water. For the purpose, different methods are often used to recover lactic acid from water. Compared to other methods, adsorption has some advantages such as high efficiency and easy handling and low capital and operation costs [2,3].

2. Materials and Methods

Lactic acid solutions were prepared by dissolution of the initial acid concentration of approximately 2%, 4%, 6%, 8% and 10% (w/w) in distilled water. In the experiments, the volume of lactic acid solution of 5 mL was used. Firstly, the optimum adsorption time was determined by using Amberlite IRA-400 of 0.1 g and initial concentration of lactic acid solution of 10% (w/w). The optimum adsorption time was determined as 180 min. Then, the effect of initial concentration of lactic acid was examined at the optimum adsorption time. And then, the effect of amount of adsorbent was detected by using Amberlite IRA-
400 of 0.1, 0.2, 0.3, 0.4 and 0.5 g and initial lactic acid concentration of 10% (w/w). Finally, the effect of temperature was investigated at the different temperatures of 25°C, 45°C and 65°C. The batch adsorption experiments were carried out in a thermostatic shaker bath at 150 rpm. The adsorbent was separated from solution by filtration. The concentrations of acid before and after adsorption process were determined with titration method by using 0.1 N NaOH.

3. Results

Figure 1 shows the effect of initial lactic acid concentration, Amberlite IRA-400 amount and temperature on the adsorption. It is obvious from Figure 1 that the adsorption capacity increased by increasing the initial lactic acid concentration and decreased by increasing the amount of Amberlite IRA-400 and also, decreased slightly by increasing the temperature.

![Figure 1. The effect of initial acid concentration, Amberlite IRA-400 amount and temperature on the adsorption.](image)

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References
Removal of Ciprofloxacin Hydrochloride from Water by Adsorption with Various Adsorbents

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Keywords: Ciprofloxacin Hydrochloride, Adsorption, Montmorillonite, Amine Montmorillonite, Activated carbon.

Abstract

In this study, the removal of ciprofloxacin hydrochloride, a fluoroquinolone antibiotic, by using various effective adsorbents such as montmorillonite, amine montmorillonite and activated carbon was investigated. Adsorption experiments were performed to determine and compare the adsorption capacities of adsorbents. The adsorption capacities of adsorbents were examined at different initial concentrations of ciprofloxacin hydrochloride. The adsorption capacity values of activated carbon were found higher than montmorillonite and amine montmorillonite. Also, the adsorption capacity values of amine montmorillonite were found higher than montmorillonite. For the solution having initial ciprofloxacin hydrochloride concentration of 4 mg/L, the maximum adsorption capacities of adsorbents were determined as 1.8591 mg/g for activated carbon; 1.6654 mg/g for amine montmorillonite and 0.6037 mg/g for montmorillonite. In addition, Langmuir and Freundlich isotherm models were applied to express the adsorption process. Both isotherm models provided best fitting to the experimental data for all adsorbents because of very high values of R².

1. Introduction

Ciprofloxacin hydrochloride, one of the most used fluoroquinolone antibiotics, is used for human and veterinary treatment. It is commonly found in the wastewaters and surface waters with concentrations of several hundred ng/L. It is also found in higher concentrations up to 150 μg/L in the effluents from hospitals. Nowadays, it can be occur in various natural environments due to the increase of global needs and inconvenient discharge. If it is present in drinking water, it can be cause headaches, tremors, nervousness, diarrhoea, nausea, vomiting etc. Its presence in higher concentrations in drinking water can be cause more serious adverse effects like elevation of liver enzymes, acute renal failure, thrombocytopenia, eosinophilia and leucopenia etc. For these reasons, it is very important for the removal of ciprofloxacin hydrochloride from water [1-2].

2. Materials and Methods

In experimental section, initially, the effect of adsorption time was examined and adsorption time required to equilibrium was determined as 200 min for all adsorbents. The adsorption experiments have been performed by shaking glass flasks including 20 mL ciprofloxacin hydrochloride and amount of adsorbents of 0.04 g in a shaker bath for 200 min. These samples were centrifuged for 10 min, and were filtered through a 0.45 μm filter. The
concentrations of ciprofloxacin hydrochloride before and after the adsorption experiments were analyzed by a UV/VIS spectrophotometer (Varian Cary 100) at a wavelength of 276 nm. The calibration curve was established with 8 standards between 1-8 mg/L with the value of correlation coefficient $R^2$ of 0.9996.

3. Results

The adsorption capacity values of activated carbon were found higher than montmorillonite and amine montmorillonite. Also, the adsorption capacity values of amine montmorillonite were found higher than montmorillonite. For the solution having initial ciprofloxacin hydrochloride concentration of 4 mg/L, The maximum adsorption capacities of adsorbents were determined as 1.8591 mg/g for activated carbon; 1.6654 mg/g for amine montmorillonite and 0.6037 mg/g for montmorillonite.

![Figure 1. Comparison of the adsorption capacities of adsorbents for the removal of ciprofloxacin hydrochloride.](image)

References


Comparison of Centralized and Source Separation System for Sustainability

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Keywords: Centralized system, source separation, ECOSAN, sustainability, SWOT

Abstract

In recent years, water management and sustainability have become increasingly important issues. Because of increasing population and decreasing resources, it is necessary to use existing resources more effectively. Since water is the most important thing for the continuation of life, water management is extremely important. Wastewater is another important subject for water management. Nowadays, source separation is evaluated for wastewater treatment instead of centralized systems, because domestic wastewater components have different properties and can be reused for different purposes according to them.

1. Introduction

Water is vital for the sustainability of life. Although Earth is comprised mostly water, fresh water resources are 3% of total water resources and accessible freshwater resources are only 0.06%. For this reason, many country has trouble for reaching to water and people consume unclean water. According to researches, water shortage will increase with time and various problems are came up. Water availability, property and pureness must be preserved in order to prevent the occurrence of problems and protect the presence of water(Ahuja, 2014).

The centralized system is used for many years for treatment of domestic wastewater. Domestic wastewater contains different fractions and these fractions are mixed in sewer system, after mixing wastewater is treated in centralized treatment system. When wastewater is mixed, wastewater has big volume and it diluted. Mechanical, biological and physicochemical processes are used for treating to wastewater, before wastewater is discharged in receiving environment. Mixed wastewater contains pathogens, nutrients, chemicals, pharmaceutics (in other words micropollutants or emerging pollutants) but centralized system does not design to removal new pollutants such as chemical compounds, for this reason there is a problems in the recovery of nutrients and reuse of water. Additionally, centralized system’s infrastructure is not flexible and it has high investment cost(Remy & Jekel, 2008). If the centralized system disadvantages are listed:

- Insufficient treatment or noncontrollable discharge of wastewater
- Nutrients, pharmaceutics etc. pollution in water
- Eutrophication and environmental harm
- High investment, energy, operating and maintenance costs
- Nutrients loss
- Contaminated sewage sludge

Centralized system is occurred waste idea, it means that water is waste it does not use any purposes, but in nature, there is no waste, all materials are a part of a cycle. When the health risks , water crisis are evaluated, new approach must be considered for sustainability(Werner, Panesar, Rüd, & Olt, 2009).
A new approach is ecological sanitation (ECOSAN), it is based on closed loop system and human excreta and water are not a waste, they are source for evaluating in this system. Thanks to closed loop, nutrients is recovered, water is reused and energy is generated. Important issue for cycle is appropriate control technologies are determined, protection of human health issues need attention. If advantages of ecological sanitation are listed (Werner et al., 2009):

- Recovery of nutrients and reuse of water and generate of energy
- Protection of resources (lower water consumption, fertilizer substitution)
- Decentralized cost effective system
- Contribution of soil fertility
- Holistic approach

ECOSAN is a working principle and an important feature is the concept of source separation and every stream has different treatment techniques. Source separation streams occurs yellow water(urine), brown water (faecal matter), black water (yellow+ faecal compound) and grey water (kitchen, sink etc.)(Simha & Ganesapillai, 2017). Compared to centralized system, source separation is more effective technique for resource recovery. Grey water can be used for toilet flushing or irrigation, thus water usage can be decreased. Brown water can be used for generating energy, because of high organic matter content. Yellow water can be used nutrient recovery and they are applied to agriculture. Moreover, source separation is useful technology in order to removal of micropollutants(LeMonde Fewless, 2015).

The aim of this study is to compare centralized system and source separation system with SWOT analysis. These two system has both positive and negative sides, SWOT analysis will be used to evaluate the properties of the two systems and try to determine which system is effective for sustainability.

2. SWOT Analysis

SWOT is structural or organizational analysis technique, and it has four main topics; strengths, weaknesses, opportunities and threats. Strengths and weaknesses are composed inner conditions, opportunities and threats are occurred outer conditions. Thanks to this technique, new plans can be created by doing situation assessment (Verboncu, 2016).

References


Efforts to promote the recovery of hydrogen gas from municipal solid waste incineration bottom ash (MSWIBA) by using catalysts

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Keywords: Hydrogen, MSWIBA, Metal aluminum, Catalyst, TiO\textsubscript{2}, Sodium hydroxide solution

Abstract

The experiments were conducted to investigate the effects of TiO\textsubscript{2} addition and using Sodium hydroxide solution for enhancing hydrogen production from MSWIBA. According to the results of the batch tests, 10 % of TiO\textsubscript{2} addition promoted the hydrogen generation amount. However, 20 % of TiO\textsubscript{2} addition was not effective. When MSWIBA was mixed with sodium hydroxide solution, the hydrogen generation rate was 11.8 times higher than pure water in day 1. In total, the hydrogen generation amount was 3.4 times at the end of experiment.

1. Introduction

Approximately 4.3 million tons of MSWI residue was generated in Japan in 2016 (Ministry of the Environment of Japan, 2018). It is well known that MSWIBA includes metal Al (Saffarzadeh et al., 2016). Therefore, hydrogen is generated when MSWIBA contacts with water as per the following chemical reaction (Armstrong and Braham, 1996).

\[ 2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2 \]

TiO\textsubscript{2} promotes hydrogen generation from Al powder at the presence of water (Wang et al., 2011). And at higher pH, corrosion speed of Al increases (Chatalov, 1952). Should hydrogen be efficiently generated from MSWIBA, it can be considered an alternative source of energy. The purpose of this study was to investigate the techniques of hydrogen promotion using TiO\textsubscript{2} and sodium hydroxide solution.

2. Materials and Methods

MSWIBA sample was collected from incineration plant R of City F in Japan. It was cooled by water before sampling. The sample was sieved less than 30 mm in diameter, and the ferrous metals were removed by magnetic separation. Thereafter, the samples were air-dried. The concentration of metal Al was measured by atomic absorption spectrophotometry. The metal Al content of the bottom ash samples was about 3.8 % in average.

The hydrogen production experiments were conducted using glass vials (470 ml). 20 g of MSWIBA and 100 ml of water (L/S\textsubscript{ash} = 5) were placed in the vials and the experiments were conducted at 35 °C under agitation (200 rpm). Hydrogen generation was calculated from pressure in each vial. 5, 10, and 20 % of TiO\textsubscript{2} powder was added to each vial to examine its effect. In separate tests, the effect of 100 ml sodium hydroxide solution (1 mol/l) on hydrogen enhancement was also investigated.
3. Results

The hydrogen generation rate increased after day 2 at the presence of 10% of TiO$_2$ (Fig. 1a). In addition, the accumulated hydrogen generation amount increased 27% as compared with the original bottom ash (2nd time) that received no catalysts (Fig. 1b). In the case of 5% TiO$_2$, hydrogen generation rate and the cumulative amount were almost similar to the original bottom ash. However, in the case of 20% TiO$_2$, hydrogen generation rate and the accumulated amount even decreased. It is evident that an optimum amount of TiO$_2$ must be added for promoting of hydrogen generation. Sodium hydroxide solution also significantly increased hydrogen generation rate and the cumulative amount. On day 1, the rate was almost 12 times higher than when pure water was used (Fig. 2a). However, the cumulative amount of hydrogen generation was 3.4 times higher than the pure water scenario (Fig. 2b).

![Figure 1](image1.png)

**Figure 1.** Hydrogen promotion by TiO$_2$ addition: a) daily generation rate, and b) cumulative generation after 8 days.

![Figure 2](image2.png)

**Figure 2.** Hydrogen promotion by sodium hydroxide solution: a) daily generation rate, and b) cumulative amount after 10 days when the hydrogen generation stopped.

References


Adsorption of cationic methylene Blue (MB) dye onto natural untreated clay (NUC) : Kinetics, equilibrium and thermodynamics

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Keywords: Adsorption, untreated clay, Kinetics, Thermodynamic

Abstract

The aim of this study is to eliminate the methylene Blue (MB) from an aqueous solution by adsorption onto a natural clay from Algeria. Adsorption experiments are conducted in batch mode. The parameters examined and their studied range, respectively are initial concentration of methylène blue (50-200 mg.L⁻¹), clay dose (1.0-3.0 g.L⁻¹) contact time (2 h), pH of solution (3-12) and solution temperature (15-50°C). The results showed that the kinetics of adsorption is described by a pseudo-second-order model, with a high regression coefficient (>0.999). Adsorption isotherms of MB onto clay were determined and correlated with common isotherm equations such as Langmuir, Freundlich, Temkin, Dubinin–Radushkevich and Toth isotherm models. The Langmuir model agrees very well with experimental data, with a regression coefficient (>0.90). The thermodynamic parameters determined show that the adsorption of MB onto clay was a spontaneous and an endothermic process.

1. Introduction

The problems of water resources and pollution are increasingly on the agenda. The dye containing effluents from different industries such as textile, paper, plastics, leather, food processing, and cosmetics, receives special attention by environmentalists. Many dyes are designed for their chemical stability and do not undergo biochemical degradation readily [1]. Among all waste water treatment processes, adsorption is one of the most popular technologies and is considered as an effective, efficient, and economic method for water purification and recycling currently, and also, dyes can be effectively removed by adsorption process in which dissolved dye compounds attach themselves to the surface of adsorbents. Clays are cheaper than activated carbons and may be efficient adsorbent, because they are lamellar minerals with structure providing high specific surface areas and large adsorption capacities. The aim of this work is to study the adsorption phenomena on natural clays, of cationic dyes encountered in dyeing effluents. This study concerns the removal of methylene blue. The effects of initial dye concentration and clay dosage on MB adsorption were investigated. Kinetics and isotherm studies and thermodynamic parameters related to the process were also performed.

2. Materials and Methods

Methylene blue as typical basic cationic dye employed in this study was purchased from (Merck, Germany) Company. Table 1 represents the chemical structure and general characteristics of MB. All of the methylene blue solution was prepared with distilled water. The adsorbent used in this study is a natural clay from Algeria.
Batch equilibrium and kinetic studies

Batch equilibrium adsorption studies were carried out in a set of Erlenmeyer flasks (250 mL) with 100 mL of MB solutions at different initial concentration. The concentration of MB solution before and after adsorption was analyzed by determining the absorbance of the solution at the maximum wavelength of 665 nm using a UV–vis spectroscopy.

3. Results

3.1. Effect of initial concentration on MB adsorption

The initial concentration of adsorbate in solution provides an important driving force in overcoming mass transfer resistance between the aqueous and the solid phases [2].

Profiles for MB uptake by natural clay at various initial concentrations are shown in Fig. 1. When the initial concentration of the dye was 50, 100, 150 and 200 mg/L, the dye was completely adsorbed in 2 min. At higher concentrations, the dye was not completely adsorbed, indicating that there is a saturation limit for the natural clay above which it does not remove the dye from solution. At lower concentrations all MB present in the adsorption medium could interact with the binding sites on the surface of adsorbent so higher adsorption capacity were obtained. At higher concentrations, lower adsorption capacities were observed because of the saturation of the adsorption sites. A similar phenomenon was observed for the adsorption of methylene blue dye [3] [4][5].

![Fig. 1. The effect of initial dye concentration on adsorption rate on NUC.](image)

3.2. Effect of clay mass

In the goal to determine the required sediment quantity for a maximal removal of MB, the effect of natural clay mass on the kinetic of MB removal was studied; the experiments were achieved in one liter of solution (initial concentration of MB 100 mg/L). The effect of adsorbent dosage (0.2 g/L to 1.4 g/L) on MB dye adsorption capacity is presented in Fig. 2. The adsorption capacity was increased with adsorbent mass from 0.1 g/100 mL to 0.35 g/100 mL. Equilibrium time was lesser at higher adsorbent.
3.3. Thermodynamics of adsorption

The thermodynamic adsorption parameters determined are given in Table 1. Shows the negative values of $\Delta G^0$ and positive $\Delta H^0$ (75.5 kJ/mol) obtained indicated that the MB dye adsorption process is a spontaneous and an endothermic. The positive value of $\Delta S^0$ (0.296 kJ/mol.K) suggests increased randomness at the solid/solution interface occur in the internal structure of the adsorption of MB dye onto clay. The increase in spontaneity with increase in temperature implies that adsorption of MB on natural clay was more favorable at higher temperatures [6].

<table>
<thead>
<tr>
<th>$\Delta H^0$ (kJ/mol)</th>
<th>$\Delta S^0$ (kJ/mol)</th>
<th>$\Delta G^0$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75.5</td>
<td>0.296</td>
<td>288 K</td>
</tr>
<tr>
<td></td>
<td></td>
<td>303 K</td>
</tr>
<tr>
<td></td>
<td></td>
<td>308 K</td>
</tr>
<tr>
<td></td>
<td></td>
<td>313 K</td>
</tr>
</tbody>
</table>

**Table 1**: Thermodynamic properties of MB adsorption on natural clay.

**Adsorption isotherms**

The adsorption parameters were evaluated using several linear forms of Langmuir-1, Langmuir-2, Langmuir-3, Langmuir-4, Freundlich, Dubinin–Radushkevich, Temkin and Toth isotherm models. The adsorption equilibrium data were evaluated by the aforementioned isotherm equations. The value of $R^2$ obtained from Langmuir-1 isotherm equation (0.999), was higher than that from Langmuir-2(0.975), Langmuir-3(0.935), Langmuir-4(0.935), Freundlich (0.733), Dubinin–Radushkevich(0.980) and Tempkin (0.837) isotherm equations. This fact indicated Langmuir-1 isotherm model which assumes a monolayer coverage and uniform activity distribution on the sorbent surface, could well describe the MB adsorption on natural clay. The value of $R_L$ decreased and tended toward zero with the increase in initial MB concentration. This behavior indicating adsorption equilibrium process was close to the ideal irreversible case, not toward unity, suggesting the completely reversible case.

**Adsorption kinetics**

In order to investigate the adsorption kinetic of BM on the Natural Clay, the pseudo-first order model and the pseudo-second-order model are used. The coefficients of determination of the first-order model are less than those obtained in the case of the second-order model, and the value of $q_e$ (the amounts of dye adsorbed at
equilibrium) found, we noted that this value calculated by the pseudo-second-order model is very close to that determined experimentally. What further justifies the adsorption kinetics of methylene blue by the Natural Clay is pseudo-second-order.

### Table 2: Kinetic parameters for the adsorption of BM on the Natural Clay at pH 7.0 and 25°C

<table>
<thead>
<tr>
<th>[BM] (mg/L)</th>
<th>Pseudo-first-order model</th>
<th>Pseudo-second-order model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k₁(1/min)</td>
<td>qₑ(mg/g)</td>
</tr>
<tr>
<td>100</td>
<td>0.078</td>
<td>0.119</td>
</tr>
<tr>
<td>150</td>
<td>0.005</td>
<td>0.145</td>
</tr>
<tr>
<td>200</td>
<td>0.004</td>
<td>0.747</td>
</tr>
<tr>
<td>250</td>
<td>0.026</td>
<td>7.14</td>
</tr>
<tr>
<td>300</td>
<td>0.046</td>
<td>23.855</td>
</tr>
<tr>
<td>350</td>
<td>0.024</td>
<td>8.141</td>
</tr>
</tbody>
</table>

### Conclusion

This study showed that the natural clay used in this study can be used as solid adsorbent to remove dyes from aqueous solution contaminated by textile dyes. Its efficiency has been proven through the kinetic, isotherm and thermodynamic adsorption studies of methylene blue, considered as a reference cationic dye.

### References

Optimization of the emerging pollutant elimination by adsorption process: Application of Doehlert design

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Keywords: Water treatment, Adsorption, Vegetable waste, Experimental design, Doehlert design.

Abstract

The objective of this study is to optimize and model an adsorption process with an activated carbon, elaborate from a vegetable waste to eliminate an emerging pollutant using an experimental design (doehlert design). This waste is activated with phosphoric acid with an impregnation ratio r = 2, and carbonized at a temperature of (T = 500 °C) during 2 hours. Preliminary tests are performed to examine the performance of the activated carbon to eliminate an emerging pollutant (drug molecule). The kinetics of the adsorption showed that the adsorption is very fast and reaches equilibrium in 10 min. The elimination yield obtained is more than 70%. The study of the pH effect of the medium shows that the adsorption is favored in a neutral medium. The Doehlert design is used to study the effect of 3 factors on adsorption, there are the pollutant concentration [pollutant] = [50; 150 mg.L⁻¹], activated carbon dose = [0.5 ; 2.5 g.L⁻¹] and temperature T = [20°C ; 40°C]. The results obtained are analyzed with the JMP software. The optimal conditions obtained for a yield of 99.97% are: [pollutant]= 75ppm, AC dose= 2.36gl and T=30°C.

1. Introduction

Over the last thirty years, pharmaceuticals have been receiving increasing attention as potential bioactive chemicals in the environment (Kümmerer, K., 2009). Veterinary drugs are a potential group of chemical contaminants because they have designated to have a biological effect at very low concentrations (Arnold et al, 2014). They are considered as emerging pollutants in waterbodies, because they still remain unregulated or are currently undergoing a regularization process, and they are continuously introduced into the environment and are prevalent at small concentrations (Kolpin et al 2002). Adsorption remains one of competitive processes in polluted water treatment, and activated carbon is undoubtedly considered as universal adsorbent for water pollutants removal (Demirbas. A 2009), due to its porosity and very high specific surface area. Petroleum residues, natural coal and woods were for a long time, the main activated carbon precursor (Khezami et al 2005). Therefore, in Algeria, the oaks represent a forest capital, they cover large areas, about 40% of the Algerian forest (Alatou D., 1994). Acorn cups are residues left after the consumption of this fruit. Because of this abundance, this vegetable waste can be used as a precursor for the development of activated carbon.

2. Materials and Methods

Acorn cups are used as a precursor, washed in distilled water. It is activated with phosphoric acid [H₃PO₄]= 30%, impregnation ratio r=2 during 2h with warm-up. Carbonization was done in T=500°C for 2 hours.
15 batch adsorption tests are made according to 3 factors [pollutant], activated carbon dose, and medium temperature with respect to the doehlert plan matrix. Results are analyzed with JMP software.

3. Results

Table 1. Representative table of the doehlert matrix and the actual values of each test and their performance.

<table>
<thead>
<tr>
<th>Factor (pollutant concentration(ppm))</th>
<th>Factor 2 : AC Dose (g/L))</th>
<th>Factor 3 (temperature°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>coded value</td>
<td>real value</td>
<td>coded value</td>
</tr>
<tr>
<td>1 0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>2 +1</td>
<td>150</td>
<td>0</td>
</tr>
<tr>
<td>3 +0.5</td>
<td>125</td>
<td>+0.866</td>
</tr>
<tr>
<td>4 -0.5</td>
<td>75</td>
<td>+0.866</td>
</tr>
<tr>
<td>5 -1</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>6 -0.5</td>
<td>75</td>
<td>-0.866</td>
</tr>
<tr>
<td>7 +0.5</td>
<td>125</td>
<td>-0.866</td>
</tr>
<tr>
<td>8 0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>9 -0.5</td>
<td>75</td>
<td>+0.289</td>
</tr>
<tr>
<td>10 0</td>
<td>100</td>
<td>-0.577</td>
</tr>
<tr>
<td>11 +0.5</td>
<td>125</td>
<td>+0.289</td>
</tr>
<tr>
<td>12 -0.5</td>
<td>75</td>
<td>-0.289</td>
</tr>
<tr>
<td>13 0</td>
<td>100</td>
<td>+0.577</td>
</tr>
<tr>
<td>14 +0.5</td>
<td>125</td>
<td>-0.289</td>
</tr>
<tr>
<td>15 0</td>
<td>100</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 1. Graph of observed values according to predicted values

References


Process Parameters Optimization of Graphite-Graphite Electro-Fenton System for the Treatment of Sunflower Oil Refining Industry Wastewater

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Keywords: Wastewater treatment, electro-Fenton, graphite, vegetable oil wastewater, response surface methodology

Abstract

In this work, the results of the application of Electro-Fenton treatment (EF) over sunflower oil refining industry wastewater were presented. Effect of pH, current intensity, FeSO₄·7H₂O and %50 H₂O₂ concentration on chemical oxygen demand (COD) removal and energy consumption were investigated using Box-Behnken experimental design. Results show that water has been obtained in a dischargeable quality according to Water Pollution Control Regulation of Turkish Authorities with 99.56 % COD removal and 0.44 kWh/kg COD removed energy consumption under optimum operating conditions of pH 3.21, 1.51 A current intensity, 11.28 g/L FeSO₄·7H₂O concentration and 18.59 mL/L %50 H₂O₂ concentration.

1. Introduction

Discharge of wastewater formed by the vegetable oil treatment industry into receiving environments poses a serious threat to water resources [1]. Characteristics of wastewater include high amounts of chemical oxygen demand (COD), total suspended solids (TSS), oil and grease, phenol, heavy metals, sulfates, nitrogen and phosphates. These result in both high organic and inorganic loading into the respective wastewater treatment plants [1]. According to Water Pollution Control Regulation of Turkish Authorities, the amount of COD in the wastewater to be discharged should not exceed 200 mg/L [2]. Various treatment processes have been developed for oil removal from water, including gravity separation, cyclone separation, chemical precipitation, sorption, membrane filtration and chemical oxidation [3]. Disadvantages of these treatment applications are reported as low efficiency, long processing time, secondary pollution and high costs [3]. The Electro-Fenton system (EF), a special type of electrochemical reaction, has attracted many researchers’ attention in recent years [4]. Fenton process generates hydroxyl radicals by the reaction between H₂O₂ and Fe²⁺ ions in an acidic medium. EF process consists of adding ferrous ions with the simultaneous electrogeneration of hydrogen peroxide upon the two-electron reduction of oxygen on the cathode surface [5]. In this work, application of the EF process over sunflower oil refining industry wastewater were presented.

2. Materials and Methods

Sunflower oil refining industry wastewater was obtained from an industrial plant located in Edirne/Turkey. Batch experiments were carried out in a glass EF reactor with a working volume of 1 L using original wastewater characteristics at room temperature with a stirring speed of 400 rpm. 6 graphite electrodes with monopolar parallel arrangement were used.
with an inter-electrode distance of 1 cm in experiments. A direct current power supply (Marxlow PS 305D) working in 0-5 ampere range was used to maintain experiments at constant current intensity. Characteristics of the wastewater are given in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>pH</th>
<th>Conductivity (mS/cm)</th>
<th>Turbidity (NTU)</th>
<th>COD (mg/L)</th>
<th>Color (CU)</th>
<th>TSS (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>7.21</td>
<td>1.76</td>
<td>7625</td>
<td>10836.02</td>
<td>60134</td>
<td>28.50</td>
</tr>
</tbody>
</table>

A four factor Box-Behnken experimental design matrix was applied in order to perform multi objective optimization using Response Surface Methodology. Levels of the independent variables of EF process are given below in Table 2.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Minimum</th>
<th>Centre</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_1$ pH</td>
<td>1.00</td>
<td>3.00</td>
<td>5.00</td>
</tr>
<tr>
<td>$x_2$ Current intensity (A)</td>
<td>1.00</td>
<td>2.75</td>
<td>4.50</td>
</tr>
<tr>
<td>$x_3$ FeSO$_4$.7H$_2$O concentration (g/L)</td>
<td>3</td>
<td>9</td>
<td>15</td>
</tr>
<tr>
<td>$x_4$ %50 H$_2$O$_2$ concentration (mL/L)</td>
<td>0</td>
<td>10</td>
<td>20</td>
</tr>
</tbody>
</table>

### 3. Results

Regression models were fitted to the experimental data as shown in equation 1 and equation 2, respectively.

$$COD(\text{mg/L}) = 923 - 107.7x_1 - 56.8x_2 - 16.17x_3 - 84.7x_4 + 17.47x_1^2 + 3.09x_2^2 + 0.846x_3^2 + 12.4x_4^2 - 1.38x_1x_3 - 0.882x_2x_3$$  

(1)

$$\text{Energy consumption (kWh/kg} \ \text{COD}_{\text{removed}} = -0.550 + 0.2972x_1 - 0.0221x_2 - 0.0074x_3$$  

+0.14$x_4 - 0.0418x_1^2 - 0.00128x_2^2 + 0.0828x_4^2 + 0.0042x_1x_3 - 0.00494x_3x_4$$  

(2)

Multi objective optimization was performed in order to achieve maximum COD removal and minimum energy consumption goals. Optimum conditions were determined according to the fitted models as, pH 3.21, 1.51 A current intensity, 11.28 g/L FeSO$_4$.7H$_2$O concentration and 18.59 mL/L %50 H$_2$O$_2$ concentration and 99.56% COD removal was achieved with an energy consumption of 0.44 kWh/kg COD$_{\text{removed}}$.

### References

Epoxy Composites with Washed PS Wastes’ Pyrolysis Char Additives

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Keywords: Char, composite, pyrolysis, PS waste

Abstract
This study presents pyrolysis of PS waste (washed) and preparation of epoxy composite with pyrolysis char. In the scope of the study, PS wastes were pyrolysed in fixed-bed pyrolysis reactor at different temperatures and epoxy composite materials prepared with PS char were analyzed for mechanical, electrical and thermogravimetric properties.

1. Introduction
Polystyrene (PS) is one of the most employed aromatic thermoplastic polymer finding a wide range of application from food contact packaging to thermal insulator in buildings. European production of PS was more than $3.5 \times 10^9$ kg, and its disposal is an environmental and social problem (Plastics Europe, 2012). Pyrolysis is a suitable process for oil based material, where the plastic waste is heated in the absence of oxygen to break the long chain hydrocarbons into intermediate and small chain hydrocarbons. Epoxy resins are thermosetting polymers. Generally, epoxy composite materials are obtained from epoxy resins. The epoxy resins are produced from matrix and particles as filler material.

2. Materials and Methods
Waste PS plastics were crushed and pyrolysed at 300, 500 and 700°C with 5°C/min heating rate. Solid (char), oil and gas products were collected separately. Char samples were analysed by SEM and TGA. Accurately weighed char was added to the epoxy composites (ER) at doses of 10, 30 and 50 wt% of the epoxy, stirred for 3 hours at 2000 rpm by mechanical mixer. ASTM D638 (2002) standards were used for preparation of composite samples. Electrical properties of the ER were determined with an electrometer. Hardness tester (Shore Durometer TH 210) was used for measuring their hardness. Stretch and pressing equipment (TST-Mares/TS-mxe) were used for the stretch resistance properties. According to ASTM D570, the effect of water absorption on epoxy composites were investigated.

3. Results
According to SEM observations, all char particles has spherical structure. As the pyrolysis temperature increased, depolymerization of waste PS increased. 700°C pyrolysis char is more homogeneous compared to other samples. With the increasing temperature, the surface of char product becomes irregular due to the shrinkage of spherical structure which is caused by devolatilization For other char samples. In the pyrolysis char obtained at 300°C, aliphatic C-H peaking at 3000-2000 cm$^{-1}$ wave number, aromatic C-H at 1000-800 cm$^{-1}$ and aromatic C-C groups at 1700-1450 cm$^{-1}$ wave number were observed (Figure 1).

The elongation at break (%), tensile strength and hardness values of composites obtained from PS char were given in Table 1. As the pyrolysis temperature increased up to 500 °C, the tensile strength, elongation at break and Young’s modulus values of composites with PS char additive increased. However, the tensile strength and Young's modulus of composites were higher than raw ER for all pyrolysis temperatures.
Figure 1. FTIR spectra of char samples

Table 1. The effect of pyrolysis temperature and char doses on mechanical properties of composite samples

<table>
<thead>
<tr>
<th>Pyrolysis Temp. (°C) and Doses (%)</th>
<th>Elongation at Break (%)</th>
<th>Tensile Strength (MPa)</th>
<th>E-modulus (GPa)</th>
<th>Hardness (Shore D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw ER</td>
<td>0.721</td>
<td>86</td>
<td>6.2</td>
<td>85</td>
</tr>
<tr>
<td>Composites</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300°C (10%)</td>
<td>0.990</td>
<td>106</td>
<td>7.5</td>
<td>85</td>
</tr>
<tr>
<td>300°C (30%)</td>
<td>1.010</td>
<td>123</td>
<td>8.8</td>
<td>85</td>
</tr>
<tr>
<td>300°C (50%)</td>
<td>0.600</td>
<td>87</td>
<td>6.1</td>
<td>86</td>
</tr>
<tr>
<td>500°C (10%)</td>
<td>1.326</td>
<td>147</td>
<td>6.6</td>
<td>86</td>
</tr>
<tr>
<td>500°C (30%)</td>
<td>1.233</td>
<td>141</td>
<td>11</td>
<td>86</td>
</tr>
<tr>
<td>500°C (50%)</td>
<td>0.989</td>
<td>140</td>
<td>9.2</td>
<td>86.5</td>
</tr>
<tr>
<td>700°C (10%)</td>
<td>1.303</td>
<td>132</td>
<td>8.8</td>
<td>87</td>
</tr>
<tr>
<td>700°C (30%)</td>
<td>0.974</td>
<td>130</td>
<td>9.8</td>
<td>86</td>
</tr>
<tr>
<td>700°C (50%)</td>
<td>0.766</td>
<td>105</td>
<td>8.3</td>
<td>87</td>
</tr>
</tbody>
</table>

In Figure 2, water absorption behavior of composite samples were given graphically. For all composite samples, as the char additive ratios were increased, the absorbed water amounts increased. The amount of water absorbed in the composite with 700°C pyrolysis char was less than the other samples. The decrease in water absorption of composite samples obtained from 700°C pyrolysis char compared to other composite samples is attributed to the formation of good interface bond between resin and chars which reduces the tendency to absorbed water through capillary action.

Figure 2. Water absorption of composite samples with (a)300°C, (b)500°C and (c)700°C PS char additives

Acknowledgement

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References

Abstract

It is an important issue to meet your water needs to ensure sustainability in cities. In order to protect both good quality water resources and to meet the supply of the cities water requirements, getting necessary to reuse the water resources in city life. From this point of view, gray water is an important source of water. The volume of the gray water that from the laundries is about 26% of the domestic gray water. Surfactants are origin from detergents, used in laundry waters, and micro-plastics come from synthetic clothes. Both surfactants and micro-plastics have the potential to adversely affect the wildlife and human health through the food chain. For this purpose, some advanced oxidation methods have been investigated using by homogeneous or heterogeneous catalysts with light. The first results obtained are promising.

1. Introduction

Today, globally, inadequate energy and water resources are the most important problems that require urgent solutions. Population growth, urbanization, high water consumption, and eventually climate change are the main reasons for this. 50% of the world's population now lives in urban areas. Gray water; is defined as wastewater from bathrooms, showers, hand basins, washing machines and kitchen sinks, and pollution load is relatively low compared to other domestic wastewater (Figure 1) (Gross et al. 2007). Typically, the amount of grey water from a house constitutes 75% of the waste water volume (Hernandez Leal et al., 2011).

Detergent used in laundry waters; whitener, water softener, and surfactants are the most important components. Depending on the type of fabric (clothes, linen etc.) to be cleaned and the degree of soiling, the type and concentration of the chemicals added during the washing process may vary and therefore the laundry waters may also differ in character.
The detergents mostly use linear alkyl benzene sulphonated anionic surfactants (Cotillas et al. 2014). Surfactants and their degradation products affect the environment biologically. Surfactants that interfere with surface water and soil have the potential to adversely affect the ecosystem due to toxicity to the surrounding organisms. (Singh et al., 2002). In addition to surfactants, recently micro-plastic is an important pollutant for the aquatic environment. Synthetic plastics are widely used in the production of fabrics and clothes and in every area. Much of the wastewater generated by the washing activities are mixed with micro-plastic sewage and then into water environments (Browne et al., 2011 Rochman et al., 2015). Microplastics include any shape or plastic form smaller than 5 mm, including fibers, granules, strata, flakes, spheres and fragments (NOAA 2015) they can adversely affect human health through the food chain. In addition, due to high emission values and sorption capacities, polyester and cotton micro-filters may play an important role in the transport and fate of chemical contaminants in the aquatic environment (Sillanpää & Sainio, 2017). There are few studies on the determination of micro-plastics in wastewater from washing machines. It has been observed that oxidants such as H2O2, TiO2, periodate are very effective in deterioration of surfactant and microplastic structures by the effect of UV light. In this work, to remove the micro-plastics in the laundry wastewater by the advanced oxidation process are focused.

2. Materials and Methods

The micro-plastic and surfactant removals from laundry waste wastewaters using different oxidizing agents such as TiO2, H2O2, periodate at different doses and pH, UV-A and UV-C lamps with different light intensities of 6, 12 and 18 W. In the analyses, anionic surfactants are determined by using HCH LANGE LCK332 cuvette test and methylene blue method (MBAS method). For the determination of micro-plastic, stereomicroscope and FTIR, which are common methods in the literature.

3. Results

It has been observed that oxidants such as H2O2, TiO2, periodate are very effective in deterioration of surfactant and microplastic structures by the effect of UV light. Experiments in wastewater from domestic washing machines have shown that a single garment can produce higher than 1900 fibers per wash. This can greatly increase the level of micro plastic involved in aquatic environments. As people use the population and therefore synthetic textiles and detergents, the habitats and the lives of living creatures living in these habitats will be compromised.

References


Insights into nonlinear adsorption kinetics and isotherms of vanadium using magnetized coal-polyaniline

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Keywords: Error function; Activated carbon; Conducting polymers; Thermodynamics; Batch adsorption; Wastewater

Abstract

Remediation of polluted environment has become a major concern in the 21st. Because of its cost benefit, ease of application, and efficacy towards the removal of pollutants, adsorption technique has gained acceptance. Different adsorption isotherms and kinetics of vanadium onto magnetized coal-polyaniline (MC-PANI) are investigated under batch experiments. All adsorption parameters are determined; maximum vanadium adsorption is compared to literature. Model suitability is assessed using average relative error deviation (ARED), Marquardt’s percent standard error deviation (MPSED), the hybrid fractional error function (HYBRID), and the sum of the squares of the errors (SSE). Nonlinear models explain the adsorption of vanadium better than linear models. According to intra-particle diffusion model, the adsorption of vanadium occurs in two stages.

1. Introduction

Fresh water availability will be most challenging problem by mid 21st. The improved standards of living, and industrialisation have led to increased consumption and extraction of earthly minerals. Among these minerals are rare metals whose effect to humans are still not known; however, the available studies indicate some of these metals are more dangerous even at micro levels in water. Vanadium is a rare earth metal—its levels have been reported to increase in water in different parts of the world. Consumption of vanadium contaminated substances (1.0 mg/L) has been reported to cause diverse effect on birds, aquatic and human life [1,2].

Removing vanadium from solution is still a challenge. Different processes have been developed [3,4], however, adsorption process has been a promising mechanism towards the extraction of rare metals from wastewater [5–7]. Before applying adsorption technique—the influential kinetic and isotherm parameters must be investigated. A number of studies have investigate the removal of vanadium from wastewater; however, the design parameters are based on just linearized forms of adsorption kinetics and isotherms.

Basing adsorption parameters on linearized forms of Pseudo-First-order (PFO), Pseudo-Second-order (PSO) kinetics, Langmuir, and Freundlich isotherms is extremely misleading during the design of actual adsorption system. Nonlinear forms of both kinetics and isotherms have been proved to be accurate over linearized forms. To choose the best kinetic or isotherm that controls the adsorption process—error functions are assessed. To find adsorption kinetic parameters using linear PFO, $ln(q_e - q_t)$ is plotted against time. As the system approaches equilibrium, the fitting index is reduced since $ln(q_e - q_t)$ becomes...
extremely large. Different forms of PSO have been developed to estimate the kinetic parameters with Ho and Mckay model being the most prominent.

The dependent variables are not entirely linear over the given values of the independent variable in isotherm equations. The inverse of data weights \( \frac{1}{q_e} \) and the presence of independent variable \( C_e \) in both dependent and independent sides causes false correlation. The inversing of variables on both sides in some isotherm equations distorts the error distribution over the entire data. In some forms of Langmuir, the presence of dependent parameter \( q_e \) on both sides leads to spurious correlation. \( R^2 \) is a very sensitive parameter that can cause spurious conclusions [8]. \( R^2 \) varies with the range of independent parameter—if the range is big, \( R^2 \) will be fit; and if the range is small, fit will be poor. Adding more data points decreases the degree of freedom of a system; this favours model fit. Making conclusions solely basing on \( R^2 \) can be misleading during industrial application.

Therefore, this study assesses the applicability of linear and nonlinear adsorption kinetics and isotherms of vanadium by magnetized coal-polyaniline (MC-PANI).

2.Materials and Methods

Coal was got from Trakya (GPS: 41.141968N, 28.353888E). Iron (III) chloride, Iron (II) chloride and ammonium hydroxide were used in the synthesis of magnetic particles. Aniline (C₆H₅NH₂), ammonium persulfate and HCl were used to generate polyaniline structure. \( \text{NH}_4\text{VO}_3 \) was expended to prepare standard vanadium solution, while sodium hydroxide and HCl were expended to alter the pH and in regeneration process—all chemicals were supplied by Merck chemicals.

Coal was cleaned with deionized water and then dried for 36 h. The dried materials were then conditioned using 1M NaCl for 24 h—then sieved and washed again with deionized water, and dried for 36 h. To produce magnetic coal; 75 ml of 0.15M FeCl₂.4H₂O (1.71 g) and 150 ml of 0.15M FeCl₃.6H₂O (3.65 g) were mixed with 3 g of coal for 30 minutes at 80 °C in a conical flask under nitrogen atmosphere—afer, 50 ml of 2M NH₄OH were added rapidly to adjust the pH to about 10. The temperature of the resultant mixture was maintained at 80 0C for 1 h. The formed magnetic coal was collected by an external magnet, cleaned with deionized water and dried under vacuum for 24 h.

Magnetized Coal Polyaniline (MC-PANI)

2.7 ml of aniline solution was mixed with 50 ml of 0.1M HCl for 20 min at a temperature below 5 0C—then 3.0 g of magnetised coal were added and stirred vigorously for 10 minutes. For polymerization, 8.55 g (NH₄)₂S₂O₇ were mixed with 50 ml of 0.1M HCl, then added slowly and the resultant mixture was stirred for 5 h. To the resultant mixture, 50 ml of 1M NH₄OH was added (to neutralize) and the system was left to age for 36 h. The solution was filtered with the help of external magnet and the formed MC-PANI was washed with deionized water until neutral pH was attained, then dried in vacuum for 24 h—4.4 g of MUC-PANI were synthesized.

2.1.Characterisation

The Burker Alpha-P Fourier Transform Infrared (FTIR) spectra was utilized to study the structure of MUC-PANI before and after adsorption. Thermogravimetric Analyser—TGA (model: LINSEIS STA PT1750) was used to study the amount of Fe₃O₄ and polyaniline
formed on coal and thermal behaviour, while X-ray Diffraction, XRD and Scanning Electron Microscopy, SEM (model, JEOL/JSM-6610) were used to study the morphology of coal. The surface characteristics were assessed with Quantachrome Autosorb Brunauer-Emmett-Teller (BET) equipped with gas sorption analyser. The zeta potential was measured using Zetasizer Nano–ZS90 Instrument—Malvern at 25 °C.

3. Results

The vanadium standard solution was prepared by dissolving NH₄VO₃ in deionized water. Adsorption batch studies were assessed by agitating 0.04 g of MC-PANI with 20 ml of vanadium solution (10-100 mg/L) for 6 h at 140 rpm. Thermodynamic parameters were examined by adjusting the temperature between 10 °C and 40 °C. The pH effect was studied by adjusting the pH from 2 to 11 by adding negligible volumes of HCl and NaOH. After adsorption, the adsorbent was separated using an external magnet. Then the solution was filtered and analysed to determine the residual vanadium using Gallic acid method—the equilibrium was examined with Eq. 1.

\[ q_e = \frac{(C_o-C_e)}{m} \times V \]  

(1)

where \( C_o \) is the initial concentration of vanadium (mg/L), \( C_e \) is the equilibrium concentration (mg/L), \( q_e \) equilibrium amount of vanadium adsorbed (mg/g), while \( m \) is the adsorbent’s mass (g), and \( V \) is the volume solution.

References

Deinking of Waste Office Paper by Chemical Flotation in Recycling

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Keywords: Office papers, Deinking, Flotation,

Abstract

In this study black ink on the laser and inkjet printouts were removed from pulp by applying flotation in paper recycling. Waste office papers were shredded and disintegrated to obtain pulp. Dispersed air flotation system was used to separate ink from the pulp. CaO and NaOH were tried as deinking chemicals by which whiteness value was increased. Recycled paper was produced from deinked pulp and product quality was checked according to Turkish national standards (TSE). Although NaOH was effective, bursting strength and breaking length of the recycled paper reduced when excess NaOH was used in deinking. Considering both deinking performance and chemical cost, CaO was suggested.

1. Introduction

Office paper, packaging paper, cardboard and paper bags have been produced within the scope of paper sector (Official Report, 2012). More than 90% of the produced paper products have been produced from the hard/soft wood pulp (Şahin, 2016; Official Report, 2012). Paper demands tremendously increase all over the world and this has been adversely affecting the ecological balance due to increasing wood utilization (Virk et al, 2013; Şahin, 2013). Increasing environmental sensitivities resulted in preparation of new rules and regulations which encourages and enforces the recycling of waste materials.

2. Materials and Methods

Waste office papers were collected, shredded, soaked into water, disintegrated with a grinder and pulp was prepared. Dispersed air flotation system with 20 L volume was used for deinking. Flotation was applied without chemical, with CaO or with NaOH addition. The scum collected on the surface of flotation system was scrapped. To investigate the effect of chemical dosage, different CaO (10%) or NaOH (10%) dosages were applied at each run. Paper samples were produced from the deinked pulp and the quality of each sample was determined according to Turkish test standards.

3. Results

The quality parameters and their test values for all produced recycled paper samples after deinking process were given in Table 1. Accordingly, % dry matter, Schopper Riegler Freeness number, unit weight, thickness and opacity values of the samples, deinked with or without chemical, were close to each other. CIE Whiteness value increased from 117.1 to 130 and 129 with CaO and NaOH addition, respectively. Similarly, Iso whiteness and Iso brightness values also increased with chemicals addition in flotation deinking process. These represent the success of deinking procedure. As whiteness get closer to the reference values, that means the recycled paper ink become closer to zero.
Table 1. Comparison of recycled paper properties for different chemical deinking applications

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reference</th>
<th>Chemical</th>
<th>Test Standard</th>
<th>No</th>
<th>CaO, mg/L</th>
<th>NaOH, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Matter %</td>
<td>TS EN ISO 638</td>
<td>0.27</td>
<td></td>
<td></td>
<td>0.21</td>
<td>0.26</td>
</tr>
<tr>
<td>Schopper Riegler no</td>
<td>TS EN ISO 5267-1</td>
<td>25</td>
<td></td>
<td></td>
<td>26</td>
<td>25</td>
</tr>
<tr>
<td>Unit weight (g/m2)</td>
<td>TS EN ISO 536</td>
<td>85</td>
<td></td>
<td></td>
<td>75</td>
<td>78</td>
</tr>
<tr>
<td>Thickness (μ)</td>
<td>TS EN ISO 534</td>
<td>146</td>
<td></td>
<td></td>
<td>130</td>
<td>133</td>
</tr>
<tr>
<td>Tearing resistance (%)</td>
<td>TS EN ISO 1794</td>
<td>74</td>
<td></td>
<td></td>
<td>64.8</td>
<td>70.2</td>
</tr>
<tr>
<td>Breaking length, km</td>
<td>TS EN ISO 1924-2</td>
<td>3.28</td>
<td></td>
<td></td>
<td>3.05</td>
<td>2.66</td>
</tr>
<tr>
<td>Bursting strength (kp/cm2)</td>
<td>TS EN ISO 2758</td>
<td>1.23</td>
<td></td>
<td></td>
<td>1.08</td>
<td>1.02</td>
</tr>
<tr>
<td>CIE Whiteness D65 D65/10</td>
<td>TS EN ISO 11475</td>
<td>117.1</td>
<td></td>
<td></td>
<td>130</td>
<td>126.1</td>
</tr>
<tr>
<td>R457 D65 (Iso Whiteness)</td>
<td>TS ISO 2470</td>
<td>80.51</td>
<td></td>
<td></td>
<td>94.57</td>
<td>91.96</td>
</tr>
<tr>
<td>R457 C (Iso Brightness)</td>
<td>TAPPI 525 SCAN-PC75</td>
<td>73.38</td>
<td></td>
<td></td>
<td>86.37</td>
<td>84.44</td>
</tr>
<tr>
<td>Opacity D65 D65/10</td>
<td>TS ISO 2471</td>
<td>98.68</td>
<td></td>
<td></td>
<td>94.25</td>
<td>96.52</td>
</tr>
</tbody>
</table>

For low chemical dosage the whiteness levels, the bursting strength and breaking length values of the low dosages were high. Higher dosages of NaOH resulted in significant reductions in bursting strength and breaking length values of recycled papers. The most preferable deinking chemical should be the one which results in higher strength and which protects the fibers better (Bhat et al., 1991; Pala et al, 2004). NaOH reduce mechanical strength of the fibers and increase the resistance by affecting the hydrophobicity, and so increasing the water absorption into fibers resulting in softer paper product. Soft paper is not a preferred material for printing purposes etc. therefore CaO is a preferrable deinking chemical. Moreover, considering the chemical cost, CaO can be suggested as a result of this study.

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Membrane Distillation Bioreactors

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Keywords: Membrane distillation bioreactor, wastewater treatment, hydraulic retention time

Abstract

This paper describes a novel wastewater treatment process known as the membrane distillation bioreactor (MDBR). The MDBR process integrates a wastewater bioreactor, such as activated sludge, with membrane distillation (MD). The ability of MD to transfer only volatiles means that very high quality treated water is obtained, with total organic carbon (TOC) levels below 1 mg/L. A unique feature is that the MDBR allows for the organic retention times to be much greater than the hydraulic retention time (HRT). The MDBR has the potential to achieve in one step the reclamation obtained by the combined MBR+RO process.

1. Introduction

Microfiltration/ultrafiltration-membrane bioreactor (MF/UF-MBR) has disadvantages in filtrate quality control for some organic materials, although it requires less area due to be excluded of the precipitation tank and allowing for higher MLSS concentration, and the effluent contains negligible suspended solids and lower TOC. The retention time of the organic substances (ORT) in MF/UF-MBR is almost equal to the HRT. This means that slowly biodegradable organic pollutants cannot be efficiently retained in the MF/UF-MBR system. Various studies have been made to separate between HRT and ORT. For example, Rautenbach and Mellis (1994) applied nanofiltration (NF) to the effluent of UF-MBR, which was treated for leachate of solid waste landfill, and sent the concentrate containing the recalcitrant organics back to the MBR. This hybrid MBR system was designed to target microorganisms to acclimate organic pollutants. The disadvantage of this system is the energy requirement for both transmembrane pressure and crossflow in the external NF. Choi et al. (2005) proposed submerged MBR with NF hollow fiber membranes for solving this problem. However, the most important disadvantage of this system is that the flow rate is very low.

The membrane distillation bioreactor (MDBR) is the result of displacement of the pressure-driven membrane in the conventional MBR by the MD. The important differences between conventional MBR and MDBR are given Table 1. Theoretically, in the literature, four different MD configurations (air gap, vacuum, gas sweeping and direct contact) can be used in MDBR. In the literature, direct contact membrane distillation module, easily made and used in the laboratory, is used in MDBR studies. The heated activated sludge in direct contact membrane distillation bioreactor system and condensed water are circulated on opposite sides of the distillation membrane. The temperature difference on both sides of the distillation membrane forms the transmembrane vapor pressure which provides the passage of the water vapor on hydrophobic membrane. MDBR systems can generally be operated under atmospheric pressures in both mesophilic and thermophilic conditions (Khaiing et al. 2010).

Microporous hydrophobic membranes such as polypropylene (PP), polyvinylidene fluoride (PVDF), or polytetraethylene (PTFE) are used in MDBR. In the MD only volatile compounds such as water vapor can pass through the membrane pores and pass to the filtrate
side. Thus, the membrane acts as a selective barrier for non-volatile pollutants. Therefore, MD provides a complete removal for non-volatile organics, salts and microorganisms. The feed solution of the distillation membrane needs to be at medium temperature (30 - 80°C) in order to provide vapor pressure, which is the driving force of the process. Average flux in MD is between 2 - 15 L/m²•h (Phattaranawik et al. 2008). These flux values are much higher than the flux value obtained from NF-MBR (Choi et al. 2005).

Table 1. The differences between MF/UF-MBR and MDBR (Phattaranawik et al. 2008)

<table>
<thead>
<tr>
<th>Specification</th>
<th>MF/UF-MBR</th>
<th>MDBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Driving force</td>
<td>Pressure (preferably suction)</td>
<td>Thermal (temperature difference) on atmospheric pressure</td>
</tr>
<tr>
<td>Membrane</td>
<td>MF or UF, preferably hydrophobic</td>
<td>Porous, preferably hydrophobic MF, such as PTFE and PVDF</td>
</tr>
<tr>
<td>Phase in membrane pores</td>
<td>Liquid</td>
<td>Vapor, gas</td>
</tr>
<tr>
<td>Membrane capture of targeted compounds and microorganisms</td>
<td>For MF, small organic compounds, less than 50% of small viruses, are spores are not retained.</td>
<td>100% of the salts, non-volatile organic compounds and microorganisms are removal.</td>
</tr>
<tr>
<td>Filtration quality</td>
<td>Depends on biological activity, 3-10 mg/L TOC</td>
<td>It does not depend on the biological activity, as compared to distillation products TOC&lt; 0.8 mg/L</td>
</tr>
<tr>
<td>Inorganics</td>
<td>Salts cannot be rejected</td>
<td>The salts are rejected and removed with the sludge.</td>
</tr>
<tr>
<td>Operational time</td>
<td>Low</td>
<td>Faster</td>
</tr>
<tr>
<td>Organic (low molecular weight) and hydraulic retention time</td>
<td>ORT-HRT</td>
<td>Independently from HRT, until the organics are CO₂ or vapor, ORT→∞</td>
</tr>
<tr>
<td>Flux</td>
<td>10-30 L/m²•h (typical)</td>
<td>2-15 L/m²•h at 55°C (~TO flux)</td>
</tr>
</tbody>
</table>

In the MD process, the volatile compounds can pass through the membrane while the non-volatile compounds are completely rejected. Additionally, biological degradation can contribute to the removal of volatile compounds in wastewater. This demonstrates that MDBR has the potential to completely purify almost all organic pollutants.

The advantages of MDBR can be ranged: (i) The filtrate quality is in RO filtration quality and is biologically independent. (ii) The filtrate quality obtained in a single system with MDBR is the same as the effluent quality of the conventional activated sludge system+MF+RO or MBR+RO. (iii) The time required to take into operation is much shorter than in conventional MBR. (iv) Pollutants, especially recalcitrant organics, can be kept longer in the bioreactor for degradation. (v) Since MDBR is a system operated under atmospheric conditions, its dependence on electric energy is very low. Thermal heat requirement can be provided by waste heat or solar energy. (vi) With the average flux target of 10 L/m²•h, the energy required for air stripping applied to reduce membrane fouling can be reduced. (vii) Observation of membrane damage in MDBR is simply possible by measuring conductivity.

The comparison of MDBR with MBR+RO in terms of cost is given in Table 2. As can be seen from Table 2, both investment and maintenance costs of MDBR are cheaper than MBR+RO.

Table 2. Economical comparison of MF/UF-MBR + RO and MDBR (Phattaranawik et al. 2008)

<table>
<thead>
<tr>
<th>Heading</th>
<th>Hybrid UF-MBR + RO</th>
<th>MDBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Main Cost</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Area</td>
<td>It can be more bigger than MDBR, because it involves two processes, MBR and RO.</td>
<td>It's smaller, but it's bigger than conventional MBR (low-flux) systems.</td>
</tr>
<tr>
<td>Membranes and modules</td>
<td>It is more expensive than MDBR because it involves two processes, MBR and RO.</td>
<td>It is a process operated in atmospheric pressure.</td>
</tr>
</tbody>
</table>
Pump systems, valves and pumps | High cost due to RO pump and pumping at high pressure | It is low due to operate in atmospheric pressure.
Membrane stability monitoring system | High cost; special equipment need | It's cheaper since flow and conductivity can be monitored continuously.
Heat exchanger | Unnecessary | Heating and cooling processes are needed.

II. Energy and operating cost

| Energy resources required for operation | Only electricity | Low of waste heat, solar and low electrical energy
| Labor cost | Higher due to two processes | Lower
| Sludge disposal | Higher | Lower

III. Maintenance cost

| Higher due to higher pressure, and more equipment | Lower

MDBR is especially suitable for situations where high water quality is required and/or where recalcitrant organic pollutants need to remain in the reactor for longer to be biodegraded. This also includes industries where waste heat is present, such as pharmaceuticals, textiles and food. Additionally, MDBRs are suitable for petroleum vessels well platforms or large ship with sufficient area problems (as they provide high quality filtrate water in a single system).

Acknowledgements

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References


Ceria based electrolyte materials co-doped with rare-earth elements for Solid Oxide Fuel Cell

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Keywords: Rare earth, doped ceria, electrolyte, XRD

Abstract

Ceria-based electrolytes have attracted increased attention due to their relatively low operating temperatures. The rare-earth elements doped ceria are likely candidates as electrolyte materials for solid oxide fuel cells. The rare-earth element Er and Sm doped ceria electrolytes were synthesized through the Pechini method and characterized by XRD, SEM and FT-IR techniques. All crystallite powders that calcined at 500 °C had a cubic fluorite structure. The pellets were then sintered at 1400 °C in air atmosphere for 6h. The sintered pellets had relative density of 91%, which was in good agreement with the SEM results. The impedance spectroscopy measurements of the sintered pellets were performed in an open circuit using two electrode configurations. Effects of the co-doping with the rare-earth elements on the structural properties and ionic conductivity were compared to the singly-doped ceria.

1. Introduction

Fluorite structured CeO₂ (Ceria) is an electrolyte material for intermediate temperature solid oxide fuel cell (IT-SOFC) [1,2]. Although yttria stabilized zirconia (YSZ) operated at ~ 1000°C is still the favored electrolyte material; Ceria is considered as an alternative electrolyte material and could operate at lower temperatures (<800 °C). The ionic conductivity of ceria is approximately an order of magnitude greater than that of YSZ for comparable doping conditions and especially when its nano-crystalline nature is maintained. However, Ceria is not a pure ionic conductor but has electronic conduction (σₑ ≈ 10⁻⁵ S/cm < 800°C) [1]. Among the various dopants studied, gadolinia doped ceria (GDC) and samarium doped ceria (SDC) have been reported to have the highest ionic conductivity [3]. In the present paper, RE (RE = Sm³⁺ and Er³⁺ ) doped ceria based Ce₀.₈Sm₀.₂₋ₓErₓO₁.₉ materials were prepared and characterized. This research is intended to study the structure and electrical conductivity of RE doped and co-doped ceria.

2. Materials and Methods

RE (RE = Sm³⁺ and Er³⁺ ) doped ceria based electrolytes were synthesized using the Pechini method. All starting materials used were highly pure: cerium (III) nitrate hexahydrate, Ce(NO₃)₃·6H₂O, samarium (III) nitrate hexahydrate, Sm(NO₃)₃·6H₂O and Er(NO₃)₃·5H₂O as the raw materials. Nitrate salts were dissolved in distilled water individually and the individual cation solutions were then mixed together in a glass beaker. More details about the Pechini method are reported in our earlier work [4].
3. Results

Figure 1. XRD patterns of a) Ce$_{0.9}$Er$_{0.1}$O$_{1.95}$, b)Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$, c) Ce$_{0.8}$Sm$_{0.15}$Er$_{0.05}$O$_{1.9}$, d) Ce$_{0.8}$Sm$_{0.10}$Er$_{0.10}$O$_{1.9}$, and powders calcined in air at 500 °C for 4 h.

Figure 1 displays the X-ray diffraction patterns of Ce$_{0.9}$Er$_{0.1}$O$_{1.95}$, Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$, Ce$_{0.8}$Sm$_{0.15}$Er$_{0.05}$O$_{1.9}$, Ce$_{0.8}$Sm$_{0.10}$Er$_{0.10}$O$_{1.9}$ samples with the fluorite structure. Sm- and Er-doped ceria, Sm/Er co-doped ceria ceramics calcined at 500°C show that the powders contain only a cubic fluorite structure.

Figure 2. SEM micrographs of the fracture surfaces of the Ce$_{0.9}$Er$_{0.1}$O$_{1.95}$ pellets sintered at 1400 °C for 6 h in air

Figure 2 shows the SEM micrographs of the surface of the sintered Ce$_{0.9}$Er$_{0.1}$O$_{1.95}$ sample. There are no pores observed on the sample surface, which is consistent with the measured density of the sintered pellet.

References

The Effects of Green Roof Application on Urban Life for Water and Energy

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Keywords: Green roof, Cost-benefit analysis, Energy, Sustainability, Urban life, Water

Abstract

In today's cities, industrialization and population are rapidly increasing. At the same time, environmental problems such as climate change and water shortage, which are the result of global warming due to increase in carbon emissions and other greenhouse gases (GHG), are increasingly felt. The green roof is emerging as an ecological method to support the sustainability of life in fast-growing cities. The green roof reduces the energy footprint of buildings by reducing energy consumption through insulation. It also helps water management, preserving the natural environment and raising the quality of life. In this study, the benefits of water and energy that green roof systems can provide to urban life have been tried to be revealed by cost-benefit analysis supported by the literature.

1. Introduction

Because of rapidly increasing population, quality of life and migrants due to business need, the need for housing and business areas in cities arises and buildings have to be built for them. However, this situation causes the green areas in and around the cities to turn into concrete structures. This leads to many of problems, such as the reduction of natural habitats in the environment and the increase in the use of natural resources for increasing population needs.

More than one million people live in more than 300 cities in the world, and in 21 megacities, the population is more than 10 million for a single city, and about 50% of today's human population lives in cities. It is anticipated that this density will reach 60% by 2030, and 82% for developed countries. Urban habitats occupy only 2% of the Earth's surface, but account for 60-80% of energy consumption and 75% of carbon dioxide emissions. Rapid urbanization and severe environmental pressures on the ecosystem continue to pose an increasing threat to human health and sustainability (Lee, Hancock, & Hu, 2014).

Due to increasing environmental problems such as global warming, drought, environmental pollution and depletion of natural resources, the world needs to develop new approaches to the concepts of development and urbanization. For the continuity of life, more and more environmentalist lifestyles have become a necessary requirement. The concept of sustainability consists of ecological, economic and social objectives that will provide an environmentally friendly life, without compromising the ecosystem balance, and even a solution to improve the quality of the environment for the preservation and sustainability of living assets.

Sustainable urban life has a need to be a principle that of being able to meet its own needs within the production-consumption cycle, waste production, energy use, and water use. The
green buildings that have green roofs, which are the building blocks of sustainable cities, are buildings with the least impact on the environment. The eco-city together with green buildings aims to protect the green areas in the cities and improve the environmental footprints of the buildings.

The energy consumption of city buildings determines the climate. The energy consumed in the building is for warming in cold climates while it is for air conditioning in warmer climates. For this reason, making buildings more energy efficient is important for decreasing city energy consumption (Addanki & Venkataraman, 2017).

Green roofs are costly systems as the first installation when compared to traditional roofs (Garrison et al., 2012). However, when compared over their lifetime, they are able to meet this cost because they have a longer life than the traditional roof. In addition, they supply other environmental benefits; such as the reduction of energy consumption of the buildings, and water management that helps water shortages, and stormwater effects. In this study, the aim is to give an example of the environmental benefits provided by the green roof. It is calculated how much economic benefits would be made with the installation of the green roof systems over existing buildings.

2. Materials and Methods

A scenario was created for a 5-story apartment building with 100 m² area and a single-story building with 100 m² area for Gebze, Turkey. It was compared with traditional and 15 cm extensive green roof in which is covered with irrigation and maintenance-free plant.

3. Results

Table 1. Comparison in Traditional Roof and Green Roof

<table>
<thead>
<tr>
<th>Annual-Totals</th>
<th>One-story building</th>
<th>Apartment building</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Traditional roof</td>
<td>Green roof</td>
</tr>
<tr>
<td>Heating cost (€/year)</td>
<td>659,5</td>
<td>395,6</td>
</tr>
<tr>
<td>Cooling cost (€/year)</td>
<td>53,1</td>
<td>31,8</td>
</tr>
<tr>
<td>Water usage cost (€/year)*</td>
<td>223,6</td>
<td>161,6</td>
</tr>
</tbody>
</table>

*amount of the water was calculated only considering kept one on the green roof

With this study, the green roof can provide economically significant savings in urban life for energy and water management. Green roofs can reduce the water load reaching the infrastructure by holding the rainwater, prevent natural disasters such as floods, and protect freshwater resources. At the same time, it will provide significant savings in energy and natural resources used for heating and cooling purposes.

References


Enzyme Activity Test and Antimicrobial Activity From Fermentation of Pineapple Fruit (*Ananas comosus* Merr.)

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**Keywords**: Enzyme Activity, Antimicrobial, Fermentation, Pineapple fruit

**Abstract**

Food is an essential requirement for everybody to growth and in sustaining life. However, if in the process of fulfillment there is an error will cause in infection or disruption in the digestive system. The microbial infection is the entry of microbes into body, then can into the body defense system and breed in the body. The method used is the enzyme activity test by using spectrophotometer and screening enzyme, resistance to acid and pathogenic bacteria activity test. A pineapple fruit (*Ananas comosus* Merr.) which has been fermented pH measured by using pH universal indicator obtained pH value is 4.0. The Fermentation process of pineapple fruit (*Ananas comosus* Merr.) was done different incubation time at 36 hours and 48 hours. After the calculation of bacterial isolate of pineapple fruit (*Ananas comosus* Merr.) with code 136 and 148 obtained the number of colonies from the isolate are $27.10^7$ cfu/ml and $16.10^7$ cfu/ml. The Gram staining test was performed to view microscopically the bacterial form of the sample was Gram negative bacteria for 136 and Gram positive for 148. The resistance to acids for bacteria isolate 136 and 148 can survive at pH 3.0. The screening enzyme results obtained for each isolate 136 and 148 with colony diameter of 2 mm and obtained clear zones for each isolates are 13 mm and 10 mm so that, the enzyme activity obtained for each isolates are 6.5 and 5. The bacteria isolate 136 has an enzyme activity value is 1.38532 units/mL with protein content is 0.33840 mg/mL and specific enzyme activity is 4.09374 units/ mg while for the sample of isolate 148 has an enzyme activity value is 1.5203 units/mL with protein content is 0.46840 mg/ mL and specific enzyme activity is 3.24574 units/ mg.

**1. Introduction**

The foodstuffs can act as an intermediate or substrate for the growth of pathogenic microorganisms and causes other. Infectious diseases are quite dangerous such as typhoid, cholera, dysentery, or tbc, easily spread with foodstuffs. Health disorders, especially stomach disorders due to food caused, due to food, allergies, lack of nutrients, poisoning of chemicals, plants or poisonous animals; toxins produced by bacteria (Siagian, 2002). High biodiversity provides a great opportunity to get microorganisms that are pathogenic in food, isolation and identification of pathogenic microbes in food products is still difficult because various types of contaminant bacteria including indigenous bacteria, while the number or concentration of pathogenic bacteria is relatively small. So that, the most conventional methods use selective enrichment methods, even if necessary through pre-enrichment stages considered less effective and efficient (Olsen, 2000).
2. Materials and Methods

Materials

pineapple fruit (*Ananas comosus* Merr.), MRS agar (Merck), Nutrient broth (Merck), Nutrient agar (Himedia, India), NaCl 0.85%. HCl. NaOH. Aguadest, casein. skim milk (Indomilk), tyrosine, TCA, Follin reagent, phosphate buffer, glyserol. MgSO₄, Tris pH 8, aquabidest (ddH₂O), spritus, safranin, iodine, crystal violet.

Methods

This work includes 3 steps, the first is Fermentation and isolation pineapple fruit (*Ananas comosus* Merr.) the samples grown in agar nutrient medium and incubated for 24 hours and temperature at 37 °C, the second, identification of BAL morphology and antimicrobial activity test and the last, protease enzyme activity test with screening protease enzyme and spectrophotometer UV-vis.

Results

Pineapple fruit (*Ananas comosus* Merr.) which has been fermented to measure its pH value using a universal pH indicator obtained pH value of 4.0. generally the pH value of foodstuffs ranges from 3.0 to 8.0. most microorganisms grow at a pH of around 5.0 to 8.0, so only certain types are found in foods that have low pH values. All of the bacterial not acid resistant such as proteolytic bacteria, rod-shaped gram-negative bacteria, cannot grow on acidic foods such as fruits, pickles or carbonated drinks (lemonade) or acid fermentation products such as yogurt, cheese and saukerkraut. some of samples is planting of bacteria done using streak method. This method is used to obtain pure microbial cultures that are not successfully grown on solid media and can only grow in liquid media is shown on Fig 1.

As shown by Fig 1, the result of Gram staining test showing that the bacteria shape as bacil and has red colour, because Gram-negative bacteria will lose the violet crystalline dye after washing with alcohol and when given a counter dye, with water coloring agent fuchsin or safranin, it will appear red. So that, the type of bacteria obtained was Gram negative bacteria for 136 and Gram positive for 148.

The acid resistance test was carried out on both isolates, isolates 136 and 148, where both bacterial isolates were tested for their growth ability in liquid nutrient broth media which had varied pH values from pH 2.0 to pH 6.0. At pH 2.0 there is very little turbidity from the media when compared to pH 4.0 and pH 5.0. whereas at pH 3.0 the turbidity of the two isolates was quite turbid compared to pH 4.0 and pH 6.0. From the pH range that has been
carried out, it can be concluded that Gram negative bacterial isolates with the highest turbidity levels are found at pH 3.0. This shows that the ability of pathogenic bacteria to develop in the digestive tract is quite high at pH 3.0.

At the time of screening the enzyme using agar nutrient medium added with 1% skim milk as a substrate of the protease enzyme. The results of enzyme screening obtained in this study can be seen from table 1.1 below:

**Table 1.1 Activity Test for Protease Enzymes by Screening**

<table>
<thead>
<tr>
<th>Bacteria isolate</th>
<th>Diameter of colony</th>
<th>Clear zone</th>
<th>Enzyme activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>136</td>
<td>2 mm</td>
<td>13 mm</td>
<td>6.5</td>
</tr>
<tr>
<td>148</td>
<td>2 mm</td>
<td>10 mm</td>
<td>5</td>
</tr>
</tbody>
</table>

The screening results obtained for isolates 136 and 148 with colony diameter of each isolate were 2 mm and 2 mm obtained clear zone for each isolate of 13 mm and 10 mm. So that, the enzyme activity obtained is for each isolate only 6.5 and 5. so that of the two isolates that have the highest clear zone with enzyme activity of 6.5 after an incubation process for 72 hours at 37 °C was 136 isolate. The thing caused because it has sufficient ability to make changes to proteins into peptide compounds and amino acids dissolved in the bacterial growth medium.

The bacterial isolate 136 has an enzyme activity value of 1.38532 units / ml with the resulting protein content of 0.33840 mg / ml. So that, the specific activity of protease enzyme for sample 136 was obtained quite well because the isolate had a good ability to hydrolyze the substrate from casein which was used to see the ability of the isolate to produce protease enzyme, which was 4.09374 Unit / mg. Whereas isolate 148 also had enzyme activity which was quite good when compared with isolates136 because the results of the study obtained an enzyme activity of 1.5203 units / ml with the resulting protein content of 0.46840 mg / ml. So that, the calculation results for the specific activity of the enzyme was 3.24574 Unit / mg.

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Comparing the European Union and Turkey Plastic Recycling Strategy

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Keywords: Plastics, Recycling, EU, Turkey, Strategies

Abstract

Plastics produced in petroleum and petroleum products are materials (PET plastics, HDPE plastics, PVC plastics, LDPE plastics, Polypropylene plastics) that can be formed with various elements such as hydrogen, oxygen and nitrogen which bind to Carbon in the structure and irreversible deformation when broken (Yer-Su, 2018). Turkey, the world's seventh, is the second largest producer of plastics and Europe (Sezgin vd., 2017). Compared to the first three months of 2017, the production of plastic products reached 3 million 477 thousand tons and 13 billion 641 million dollars in the same period of 2018. It is predicted that the production of plastic products will increase by 10.3% in quantity in 2017 and has been increased up to 10.1 million tons in 2018 (Pagev, 2018). Turkey annually about 31 million tons of waste is produced, it is known that this amount is about 3 million 900 thousand tons of packaging waste. The recycling rate of packaging, which was 37 percent until 2010, has increased to 61 percent after 2014, when approximately 2.5 million tons of these wastes could be recycled in 2016. Plastic wastes, which make up 8-12% of urban waste, have been stated as 100-160 million tons/year in terms of production all over the world. Published by the Ministry of Environment and Urban Development and by the National Waste Management Action Plan (2016-2023) in Turkey in 2014 to 4 million tonnes of packaging waste it has occurred. While a significant portion of these wastes are stored, some are converted to energy or other chemicals, while 2.4 million tonnes are collected separately and recycled (Yapıcı vd., 2018) 2015 80.8 kilograms per capita consumption of plastics in Turkey, which reaches 90.1 kilograms in 2018 has increased by 11.5% over 3 years. The same report annually 9.6 million tons of plastic are produced in Turkey, it is used as 2.2 million tons of packaging waste, it is stated that the recovery of 501 thousand tons. In the world, 300 million tons of plastic are produced annually (AA., 2018). At 2015, in Turkey produced 25.8 million tonnes of waste, 20 percent of the amount produced is expressed as part of the packaging waste. 1 million 300 thousand tons of these wastes have been certified by authorized organizations and they have been recycled (Pagev, 2018). 1698 waste disposal and recovery facility in Turkey last year and have kept operating. 44 million tons of waste per year is disposed of at regular storage facilities and 33 million tons of this waste is recycled at recycling facilities (YeniŞafak, 2018) Turkey is about 31 million tonnes of waste produced annually, it is known that the amount is about 3 million 900 thousand tons of packaging waste. It is stated that only about 2.5 million tons of these wastes can be recycled in 2016, and the recycling rate of packaging, which was 37 percent by 2010, increased to 61 percent after 2014 (BST, 2017). This statistic concerns only the part of the plastic that is produced. Researchers, according to the European Statistics Agency data have stated that less than 1 percent of waste is recycled in Turkey. Turkey has been realized for less than 1 percent of the waste recycling rates in the United States is as high as 35 percent.
Plastic production in the world has increased about two hundred times from 1950 to 2015. In Europe, 1/3 of total plastics production is recovered in 2014, the other one is collected in deponyl areas and the rest is recovered as energy. In Europe (member states), 65% of total packaging waste is recycled in 2014, only 40% in plastic packaging. Every day a large amount of plastic waste (5-13 million tonnes/year) is leak in the seas and in the ocean. Plastics that can last for too long without decay lead to degrade the nature in the world that is life-supporting ecosystem. The European Union form european strategies for plastics in the cyclical economy nowadays. In these strategies, he is working on new measures to reduce the amount of disposable plastics (beverage bottles, plastic bags, paper handkerchief, cigarette filter, etc.) at sea (EC, 2018). The European Union is developing strategies for plastic recycling, Turkey's strategies developed in the light of these developments, it was comparatively investigated in this study.

References
Abstract

The textile industry, which has grown at a fast pace, is also on the agenda with its environmental impact as well as its current production dimensions. World Trade Organization (WTO) has established 2013, according to data from the textile and ready-wear sector in the total exports of the world is 766.15 billion dollars, 27.6 billion of it belongs to Turkey (TTSIS, 2014). The high volume of chemicals and wastewater used in parallel with the large business volume make this business environment one of the risky industries in terms of environment. About 0.08-0.15 m³ of water is used per kg of fabric produced (Moustafa, 2008) and 1000-3000 m³ of fabric is processed when 12-20 tons of fabric is processed per day (Pagga and Brown, 1986; Al-Kdasi et al. 2004). Reactive dyes are used intensively in the dyeing of cellulose fibers and protein fibers in the textile industry (Ghaly et al., 2014). Acidic dyes applied at high pH to denature protein fibers form dye molecules that are insoluble on the fiber by chemical reaction. These acidic paints contain azo groups (-N=N-) in their centers. The textile industry produces large quantities of liquid wastes containing organic and inorganic compounds. except for the part that is attached to the fabric during the dyeing process, the dye is washed and mixed with the wastewater (Dyes and Pigments, 2010). Textile wastewaters contain trace metals (Cr, As, Cu, Zn, etc.) which can be harmful to the environment in such a significant amount as the paint content (Eswaramoorthi et al, 2008). The textile industry wastewaters inhibit the life of phototrophic organisms by reducing the water penetration of sunlight in receiving water environments. In addition, suspended solids and oils dissipate in the air-water interface, which significantly inhibits the oxygenation of water. Physico-chemical treatment processes such as flocculation, coagulation and ozonation are mostly used in the treatment of wastewater of textile industry. In addition, nitrogen, phosphorus and organic matter are removed by biological treatment processes. However, in economically suitable biological treatment processes, the dye present in the structure of the wastewater can be purified by using long waiting periods or without being sufficiently treated. In the literature, a lot of aerobic-aerobic biological processes have been carried out in which the dyes are removed and high removal efficiency (Ferraz et al., 2011; Frijters et al.,2006). AZo dyes removal produce aromatic amines in anaerobic conditions, the compounds are colorless, but it's still toxic. However, it is possible to break down these compounds by physicochemical processes. In this study, paint wastewater containing dye was processed in different anaerobic processes and dye degradation was studied. However, organic matter load and color removal before physico chemical process were targeted. An anaerobic fermentation and methanation reactor was used in the study. In the study, the average color reduction in the fermentation reactor in HRT 3 days was determined as 61% (Pt-Co) and the maximum removal was 86%. in the methane reactor, these values averaged 35% in color reduction and 74% in maximum
value, respectively. The color reduction due to reactors related to the subject is given in Figure 1. as Pt-Co.

![Figure 1. Color Decreases in Different Anaerobic Processes](image1)

The absorbance changes of raw and treated wastewaters in the reactors can be seen in Figure 2.

![Figure 2. Absorbance changes in different anaerobic processes](image2)

Change in organic matter at reactor effluent was investigated, also. In the methane-forming reactor, the removal efficiency increased due to the retention period, while the removal efficiencies remained low as the acidification reactors did not work for the removal of the organic substances. The change in the removal efficiencies of organic matters according to their retention times is given in Figure 3.
The study also examined according the time change in total organic carbon and gas products.

References

A Study on Numerical Simulation of Contaminated Site Capping

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Keywords: Contaminated soil, capping, zeolite, alum sludge, finite element analysis

Abstract

Contaminated soils can cause severe risks for the human health and the ecosystem. Therefore, soil contamination is one of the major global environmental concerns. The increasing concerns about soil pollution have led to the development of various remediation techniques. These remediation techniques briefly include the transfer of contaminated soils to other places for final treatment or disposal; confinement of contaminants in place; and destruction of contaminants in place [Lombi et al., 1998; Zhang, 2009].

When the contaminated soil needs to be isolated from the environment without removing or destroying the contaminants, a cover material called cap is placed over the contaminated soil. Capping is an in-situ remediation technique that aims at preventing the spread of the contaminant, keeping people and wildlife from coming in contact with the contaminated material, and creating a land surface that can support vegetation and/or be used for other purposes [EPA, 2005; URL-1].

In order to ensure that the contaminated soil is isolated from the environment, caps are generally composed of various components. The most important soil properties that must be considered in a cap design are the shear strength and hydraulic conductivity of the soil. In this study, due to their high shear strengths, low hydraulic conductivities and high contaminant removal abilities, alum sludge and zeolite are examined to be used as capping materials. Two-dimensional finite element analyses of a typical contaminated site are carried out to investigate the engineering behaviors of alum sludge and zeolite versus traditional capping materials. The finite element analyses are performed using PLAXIS, and the results are discussed in terms stability and settlement values.

References

Microplastics in Sediments of the Golden Horn Estuary (Halic), Istanbul, Turkey

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Keywords: Microplastics, sediment, marine litter, Golden Horn

Microplastics are small particles which consist of the degradation of large plastic pieces. Although not officially recognized, the millimetric range of dimensions is widely used to define the microplastics [GESAMP, 2015]. As a result of the assessments made, particles smaller than 5 mm are usually regarded as microplastic [Thomas et al., 2014; Cauwenberghe et al., 2015; GESAMP 2015; Anderson et al., 2016; Auta et al., 2017]. They have been accepted as an important threat for the aquatic ecosystem due to their persistence, toxic potential, ubiquity and absorption of organic substances [Song et al., 2015]. Microplastics can accumulate in the sediments. Furthermore, when the fact that they can be consumed by the marine organisms and enter the food chain is taken into consideration, it became necessary to determine their quantities and chemical structures [GESAMP, 2015].

In this study, the preliminary data of the survey on the microplastic pollution in the sediments of the Golden Horn Estuary (Halic), Istanbul, Turkey was discussed. As known, estuaries, which are transitional zones between rivers and seas, are known as the important ecosystems. They are typically rich in biodiversity. The Golden Horn Estuary is a hornshaped water body that connects the Alibeykoy and Kagithane Rivers to the Bosphorus strait. Over the years, the pollutant inputs from the industrial and domestic wastewaters resulted in water and sediment pollution in the Golden Horn Estuary [Coleman et al., 2009]. At the beginning of 1997, Istanbul Metropolitan Municipality started a rehabilitation project for the Golden Horn. After this date, the pollutant inputs from the industrial and domestic wastewaters into the Golden Horn were reduced by the various actions taken. In our study, the seasonal variations of microplastics in the sediment samples collected from the sampling sites selected along the Golden Horn between May 2017 and February 2018 were monitored. The data relating to the distribution of microplastics (%) in different size fractions within the sediment samples were reported.

Acknowledgement

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References


Assessment of the Geotechnical Aspect of the Use of Paper Mill Sludge as Landfill Cover Material

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Abstract

Every year, millions of tons of paper are produced in the world, which generate a huge amount of waste sludge [Monte et.al, 2009]. As stated by Lacour [Lacour, 2005], the global production in the pulp and paper industry is expected to increase by 77% by 2020. The waste generated from the paper production and recycling industry is called the paper mill sludge (PMS). Most of the PMS is dried, spread or disposed onto landfills [Mabee and Roy, 2003; Mabee, 2001]. However, due to the required landfill fees, the increasing demand for landfill space, and the stringent regulations for their disposal, PMSs are becoming a global concern. Therefore, their recycle for several beneficial uses has now become a challenge for scientists in order to decrease the necessary area and the costs for landfill disposal, and prevent environmental concerns [Ng and Lo, 2007; Zule et.al, 2007; Moo-Young and Zimmie, 1996; Charlie, 1977]. Considering its cost effectiveness, high mechanical properties, sufficient hydraulic conductivities, and the ability to adsorb various heavy metals such as lead, cadmium and zinc, PMS seems to be a promising material for use in landfill covers [Ng and Lo, 2007; Zule et.al, 2007; Moo-Young and Zimmie, 1996; Charlie, 1977].

In this study, the geotechnical behavior of a PMS is presented when used as landfill cover material, and the results are compared with those of clay, a traditional landfill cover material. For this purpose, two-dimensional finite element analyses of a typical landfill site with two different cover materials are carried out using PLAXIS finite element program.

Keywords: Paper mill sludge, landfill cover, hydraulic barrier, finite element analysis

References

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Microplastic Pollution in the Blacksea Coast of Istanbul, Turkey

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Keywords: Microplastic, beach, marine litter, Blacksea

The most abundant plastics in marine litter have become a global problem [Frias et al., 2016; Kunz et al., 2016]. These plastic materials can easily be transported to the sea and the oceans by drainage systems, runoff, rivers, wind or human activities [Cai et al., 2018; Frias et al., 2010]. Smaller plastic pieces known as microplastics (<5 mm) can be welded from both the primary and the secondary welds. The primary sources refer to the plastics used as raw materials in the plastic industry or personal care products, while the secondary sources are used to decompose larger plastic materials by photodegradation, oxidation and mechanical abrasion [Retama et al., 2016; Nor and Obbard, 2014]. Although microplastics do not cause visual pollution, they accumulate in the water ecosystems as a result of the persistence of plastic materials and slow degradation of the environment. Moreover, microplastics can have significant environmental impact, causing toxic chemicals to enter the food chain [Antunes et al., 2018; Kunz et al., 2016]. The Black Sea coast of Istanbul has a lot of rivers. These rivers allow many plastics to reach the sea and the coast. At the same time these beaches used for recreation are exposed to plastic waste as a result of human activities.

In this study, the microplastic pollution in the beaches along the Black Sea coast of Istanbul was investigated. In the scope of the study, samples were collected from different sandy beaches (from Riva to Agva) between May 2017 and February 2018. The preliminary data relating to the distribution of microplastics (%) in different size fractions within the samples was discussed.

Acknowledgement

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References

Evaluation of the Usage of Various Capping Materials in In-Situ Capping of Contaminated Sediments

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Keywords: Contaminated sediment, in-situ capping, passive capping, active capping, finite element analysis

Abstract

Sediment is the mixture of various materials including soil particles such as silt, sand and gravel, fossil fragments, sewage, industrial wastes, chemical precipitates, and organic and inorganic materials that suspend in or accumulate on the bottom of a water body [EPA, 1993]. Due to various anthropogenic activities such as industrial or municipal discharges, petroleum spills, ship wastes, and seepage and erosion from surface mining, sediments can be contaminated by organic and inorganic pollutants [TDS-2092-ENV, 2002]. Contaminated sediment is defined as soil, organic matter or other minerals that accumulate on the bottom of a water body and contain toxic or hazardous materials at levels that may adversely affect human health or the environment [EPA, 1998]. As can be seen from the definition, contaminated sediments may cause severe risks for the human health and the ecosystem. Therefore, the management and treatment of contaminated sediments is an increasing environmental concern worldwide [EPA, 1997].

In order to prevent the unacceptable risks caused by the contaminated sediments, conventional treatment methods known as monitored natural recovery, in-situ containment, in-situ treatment, or dredging or excavation may be required [Barth and Reible, 2008; Apitz and Power, 2002]. However, as stated by Zhang et al. [2016], due to the large volumes of the contaminated sediments, remediation techniques may often be economically unacceptable. On the other hand, in situ capping is reported to be a more economical, less disruptive, and more durable sediment remediation option [Zhang et al., 2016].

In-situ capping is the isolation of contaminated sediments from the environment by covering them with a layer of clean material [TDS-2092-ENV, 2002; Zhang et al., 2016]. The primary functions of in-situ capping are physical and chemical isolation of the contaminated sediments from the overlying water column and biota, stabilization and erosion protection, reduction of contaminant flux into the biologically active portion of the sediment, and new habitat creation for aquatic organisms [EPA, 2005; Azcue et al., 1998; Reible et al., 2003].

In-situ capping of contaminated sediments is classified into two as passive and active capping. In passive capping, the contaminated sediment is covered by a clean neutral material such as clean sediment, gravel, sand, silt, and clay. In passive capping application, the cap acts as a physical barrier that does not chemically alter the contaminants [Palermo et al., 1998]. However, in active capping application, chemically reactive materials such as activated carbon, apatite, zeolite and organoclay that can reduce the mobility, toxicity and bioavailability of contaminants by changing their chemical speciation are used. With active
capping, both containment and treatment of the contaminated sediment can be provided [Knox et al., 2007; Reible et al., 2006].

In this study, two-dimensional finite element analyses of a typical contaminated sediment site are carried out to investigate the geotechnical behaviors of sand, zeolite, and alum sludge, which are chosen as capping materials. In the finite element analyses, sand is used as the passive cap, and zeolite and alum sludge are used as the active cap materials. The results of the analyses are evaluated in terms stability and settlement values, and reported in this study.

References


Assessment of Heavy Metal Contamination in Urban Soil (Tuzla District, Istanbul, Turkey)

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Keywords: Urban soil, heavy metals, contamination, ecological risk

Abstract

Many contaminants such as heavy metals are dropped or discharged in the environment because of human activities. Due to the accumulation in soil, heavy metals can cause negative effects for living organisms. Consequently, the determination of heavy metals concentration and their ecological risks in soil is very important for human health.

The majority of people live in cities. Therefore, the urban environmental quality is an important issue to be investigated. Besides, as a result of the increasing urbanization and industrialization in urban areas, urban soils are contaminated by heavy metals [Yuswir et al., 2015]. Up to now, heavy metal contaminations in urban soils around the world were studied by various researchers [Wiseman et al., 2015; Yuswir et al., 2015; Mugoša et al., 2016; Mohseni-Bandpei et al., 2017; Galitskaya et al., 2017; Li et al., 2018; Wang et al., 2018]. These researchers reported that the urban soils they investigated were contaminated by heavy metals, and assessed the ecological risk of the heavy metal contamination.

In this study, the heavy metal contamination in the soils of Tuzla District, which is located in the Anatolian side of Istanbul, Turkey was investigated. The soil samples were collected in the study area during April 2018. The concentrations of heavy metals (Cu, Pb, Zn, Hg and Cd) in the soil samples were determined using inductively coupled plasma mass spectrometry (ICP-MS). The soil contamination due to the heavy metals in Tuzla District was assessed using geo-accumulation index (Igeo), enrichment factor (EF), potential ecological risk (Er), and risk index (RI).

References


Evaluation of Safe Closure Process Alternatives for Submarine Tailings Disposal Pipelines of Mines

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Keywords: Submarine tailings disposal, risk management, dispersion model, mining wastes

Abstract

Mining industry produces huge amount of wastes during its operations. The amount of mining wastes are higher amongst other industries. Disposal of mining wastes is a problematic issue because of its excessive volume, and toxicity. Near to the shoreline of a sea, mining wastes could be disposed into the deep sea environment thorough submarine tailings disposal (STD). STD is an open ended submarine pipeline lying on a steep sea bed. Use of STD is a mine tailings disposal method keeping the mining waste on the deep sea bottom. Because of environmental concerns, to keep the waste in a deep water ambient, and to avoid its suspension and dispersion are crucial. When mine closed, STD pipeline will be still full of mining wastes, which is a very high risk for the marine environment. STD pipelines can be broken by some undesirable conditions such as landslides, earthquakes etc. Pipe brakes can cause waste leakage into the sea. Because of this reason to flush of toxic mining waste from the STD pipeline using by an inert and non-toxic material is necessary to eliminate the risk factors at the end of the mine lifespan.

In this study, various scenarios were conducted in order to minimize the risks that are caused by the breakage of STD pipes. In these scenarios, conditions that may occur when a result of cleaning of the pipes with inert and non-toxic materials alternatives, have been evaluated. In addition, the behavior of inert materials which have different densities in the receiving environment was also determined by the Visual Plumes program.

References


Reuse of Domestic Wastewater Marine Outfall after Hybrid Port Change Rehabilitation Alternatives of Diffusers with Duckbill Check Valves

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Keywords: Marine outfalls, diffuser rehabilitation, duck bill check valve.

Multi-port diffusers with orifices (simply open holes i.e. ports) are commonly used for domestic wastewater disposal near by the sea shorelines. Since outfalls are designed for a definite project lifespan, it is nearly impossible to establish their full flow rate capacity at the first stage of their operational periods. Because of this reason, clogging problems can be frequently encountered in the diffuser by receiving water intrusion thorough orifices into the diffuser. For prevention of seawater intrusion into the diffuser pipe, duck bill check-valve (DBV) can be used as a rehabilitation equipment. In this study, sets of diffusers were designed using variable diameter pipes with circular discharge ports 150mm in diameter with thick wall thickness for 30 years of project lifespan with wastewater flow rate capacities of 1.0 m³/s, and 2.0 m³/s. Then, completely DBV equipment were mounted and partially DBV equipment were mounted (PDBV) on these diffusers, and their initial dilutions were calculated for the line source. The marine environment with a horizontal bottom around diffuser was adopted as the receiving ambient and its parameters determined for density as 1025 kg/m³ and for discharge depths as 10m, 20m, 30m, 40m and 50m. The results of the study were found that circular port dilution, DBV dilution, and PDBV dilution can be changeable because of rehabilitation method. There is a critical depth ($H_{cr}$), which would be advantageous for the use of PDBV. The critical depth alternatives were discussed in this study.

References

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Multivariate Statistical Analysis of Trace Metals in Istanbul Road Dust

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Keywords: Road dust, Trace metal concentrations, Multivariate statistical analysis.

Abstract

In the recent years, the growing urbanization and industrialization in the world have been caused environmental changes such as pollution and climate. Heavy metal pollution, that comes from vehicle emissions, industrial discharges and other activities, is very fast increasing in the environment. Road dust is one of important media for reservoir or sink of heavy metals, particulate matter and other pollutants in urban areas. Solid matters, that are defined as dust, mainly contains soil, anthropogenic metallic components and natural biogenic materials. Also, the dusts, which is deposited on surfaces along roadsides, are defined as road dust and they are contaminate with heavy metals and organic materials.

In this study, trace metals concentrations such as Sb, Ba, Bi, Ga, La, Sc, Sr and W in Istanbul road dust were determined for multivariate statistical analysis. Totally 11 road dust samples were collected from different main location on the Istanbul D-100 (E-5) highway and a background soil sample from a far point away from this road of Istanbul was taken from a depth of about 20 cm. The mean concentrations of Sb, Ba, Bi, Ga, La, Sc, Sr and W in road dust were found 7.336, 144.09, 0.736, 1.545, 8.09, 2.263, 194.363 and 0.409 mg/kg, respectively. Trace metals sources were identified by using correlation and multivariate statistical analysis. According to the results of these analysis, the main sources of Sb, Ba, Sr, Bi, and W in Istanbul road dust were determined anthropogenic activities.

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References


Biodiesel Production From Microalgae in Wastewater

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Keywords: Renewable Energy, Biodiesel, Microalgae, Daily Wastewater

Abstract

Academic research and deployment projects have operated substantial technical progress in developing algae-based bioenergy in recent years, because of fuel resources overconsumption and increase in air pollution from exhaust gases. Although algae are a promising alternative source for biofuel production, the developed methods are still economically not feasible. This study summarizes findings of biodiesel production by using Soxhlet extraction and Bligh Dyer methods from attached mixed culture system that growth dairy wastewater.

1. Introduction

Biodiesel has remarked as a renewable, sustainable alternative energy and environmentally friendly fuel, although fossil fuels are nonrenewable and with continued use leads to the release of environmentally harmful gases. Further, importance of biodiesel has increased because of diminishing petroleum reserves, the high cost of fuels price and the deleterious environmental consequences of exhaust gases from fuels such as carbon dioxide and other greenhouse gases have led to a global climate change. Biodiesel is an alternative fuel derived from vegetable oils such as algae, sunflower seed (Khola and Ghazala 2012, Faried, Samer et al. 2017). In recent years, growing microalgae as biofuel feedstock have increasing interest but are still not economically feasible due to several limitations related to algal culture and high production cost (Johnson and Wen 2010). Therefore, it is significant to prepare suitable conditions for algal growth as well as to get oil by economical methods.

The purpose of this study is to explore attached mixed culture system for growing the alga as biodiesel feedstock, using dairy wastewater treatment. The reason why the selection of dairy industry waste water has significant organic matter contents. The Table 1. shows the character of the dairy industry wastewater.

Table 1. Character of the dairy industry wastewater (Barnes 1984)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>mg/L</th>
<th>Average</th>
<th>Parameters</th>
<th>mg/L</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD₅</td>
<td>40-48000</td>
<td>2300</td>
<td>Suspended solid</td>
<td>24-4500</td>
<td>820</td>
</tr>
<tr>
<td>COD</td>
<td>80-95000</td>
<td>4500</td>
<td>Phosphorus(PO₄)</td>
<td>9-210</td>
<td>48</td>
</tr>
<tr>
<td>pH</td>
<td>4.5-9.4</td>
<td>7.2</td>
<td>Nitrogen</td>
<td>1-180</td>
<td>64</td>
</tr>
<tr>
<td>Temperature (C)</td>
<td>18-55</td>
<td>35</td>
<td>Chlorides</td>
<td>48-1930</td>
<td>480</td>
</tr>
</tbody>
</table>
2. Materials and Methods

The algae used was mixed culture donated by Selçuk University. Artificial wastewater was prepared using the following (mg/L): NH4Cl, 5242; KH2PO4, 5; K2HPO4, 5; MgSO4.7H2O, 5; CaCl2.H2O, 3.4; Fe(NH4)2(SO4)2.6H2O, 1.6; H3BO3, 0.5; (NH4)6Mo7O24.4H2O, 0.4; MnSO4.H2O, 0.2805, ZnSO4.7H2O, 0.2097; CoCl2, 0.071; CuSO4.5H2O, 0.01; Thiamine-HCl, 2; Tris base, 40,2. When the chlorophyll-a and optical density values increased and reached a fixed value, feeding with the daily industry wastewater has continued. Algae have grown in 25 liters plexiglass tanks in a climate of constant ambient temperature. The daylight has simulated with the daylight lamps thereby prevent light from elsewhere. To provide and compare two different lighting conditions (18:6 hours light-dark and 24 hours of light periods) have applied. The system has fed with the daily fill-and-draw method and the harvesting process has performed as much as the amount of wastewater-fed every day and harvested algae biomass has accumulated. In the harvesting process, the microalgae from the photobioreactor have kept at + 4 °C and separated from water by settling. Soxhlet extraction and Bligh Dyer (Bligh and Dyer 1959) methods have used for obtention the oil from harvested microalgae.

3. Results

0.056 g algal oil has obtained from 10 g dry algae by Soxhlet extraction method. With the method of Bligh and Dyer, 0.17 g algal oil has obtained for a 50 ml wet sample. In the extraction experiments, it has determined that Bligh and Dyer's method is more productive than Soxhlet methods. In two different photobioreactor, the effects of different lighting periods on algal oil yield have investigated. 6.2 g of oil has obtained from two liters sample in a 24 hours light tank when 2.3g algal oil has obtained from two liters sample in 18:6 hours light: darkness tank. 18:6 hours light: darkness tank is determined to be higher yield than other. Algal oils from two tanks have compared. 6.3 ml of biodiesel have produced from 7 ml algal oil obtained from the 18:6 hours light: darkness tank whereas 4.7 ml of biodiesel have product from 6ml algal oil obtained from the 24 hours light tank. Despite the fact that biodiesel production efficiencies are different for two tanks, diesel qualities have the same characteristics according to diesel standards. The Bligh and Dyer method has been a costly method due to its high chemical use, although the yield of oil recovery is high.

References


A Study on the Impact of Noise on Anger in Young Adults

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Keywords: Noise, anger, young adults

Abstract

Noise is considered to be an environmental and health problem as it is an undesirable situation and creates negative physiological and psychological effects on people. Noise pollution is one of the most common environmental problems in the world. Industrialization, rapid population growth, unplanned urbanization, transportation, and construction activities are important factors leading to noise pollution which adversely affect the environment and human health.

Although psychological effects of noise vary from person to person, they cause behavioral disorders, anger, stress, and so on. This varies depending on the character, level, frequency, duration, etc. of the noise. Studies show that exposure to noise disturbs sleep and causes daytime sleepiness, affects performance, and increases the occurrence of hypertension and cardiovascular disease [Basner et al., 2014]. The noise, which is an environmental factor, can be effective on anger by playing a stressor role. This relationship depends on age, gender and sensitivity. It known that in older age groups there is a high correlation between noise sensitivity and anger [Ramirez et al., 2004].

In this study, it was aimed to investigate the effect of noise on anger in young adults. For this purpose, the study surveyed 473 students educating at various faculty and schools in Okan University, Istanbul, Turkey. Besides, noise measurements were taken using a sound level meter at various locations in Okan University. The relationships between noise level and anger of the surveyed university students were investigated. The data of the study were analyzed with SPSS version 21.0. According to the results of the analysis, a significant positive correlation was found between trait, state, outraged and hated anger and noise among university students. However, no correlation was found between controlled anger and noise.

References

Phosphate Removal from Wastewater by using Water Treatment Sludge

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Keywords: Phosphate removal, wastewater, water treatment plant sludge

Water treatment sludge is a solid residue generated at the water treatment plant during the treatment of potable water. In order to prevent its possible harm to the environment, this sludge should be carefully treated and disposed [Teixeira et al., 2011]. Economically efficient and environmentally friendly handling methods for the huge amounts of residual sludge generated at the water treatment plants are of utmost importance. As stated by Ahmad et al. [2016], recovery, recycling and reuse of water treatment sludge may provide a sustainable solution to the sludge management problems under stringent environmental laws. Up to now, in various research studies, reuse alternatives of water treatment sludges in wastewater treatment were reported. In the meantime, alum sludge from drinking water treatment plant was examined for its ability to remove phosphate from aqueous media by various researchers [Yang et al., 2006; Gibbons and Gagnon, 2011; Gao et al., 2013]. Results of these studies which were carried out using alum sludges generated in different countries showed that alum sludge was a good adsorbent for removal of phosphate from wastewater. In our study, phosphate removal from the aqueous solution was examined using alum sludge obtained from a drinking water treatment plant located in Istanbul, Turkey. The effects of various operating variables such as adsorbent amount, pH and initial concentration were studied. Equilibrium data were fitted to the Freundlich and Langmuir isotherm equations and the equilibrium data were better fitted to the Freundlich isotherm equilibrium. The maximum adsorption capacity (q_{max}) of the alum sludge was found to be 0.76 mg/g. The results of this study were compared with those of other studies on phosphate removal by alum sludge.

Acknowledgement

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References

Removal of Methylene Blue by Cationic Resin and Regeneration Studies

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Keywords: cationic resin, adsorption, methylene blue, regeneration, kinetics.

Abstract

Adsorption studies were carried out with methylene blue onto cationic resin as an adsorbent (Lewatit CNP – 80, weak acidic, carboxylic acid functional group, macroporous, cationic type). Effect of methylene blue concentration, temperature, pH, resin dose and shaking rate were investigated for calculating the adsorption capacity of resin. Also regeneration of resin was studied for reuse capabilities. Adsorption experiment conditions was carried out 3 – 5 – 6 – 8 – 10 pH values, 10 – 25 – 50 – 75 – 100 ppm methylene blue concentration, 25 – 30 – 40 – 50 °C temperature and 150 – 200 – 250 – 300 rpm shaking rates. Removal capacity of resin was calculated as 17 mg/g to 194 mg/g at 25 °C temperature, pH 5, in 15 minutes. The removal efficiency increases with the higher pH values upto 99,63%. The study also focuses on the adsorption capacity of the regenerated resin and reuse possibilities.
The Use of Sensors for Monitoring Particulate Matters in Urban Air of Istanbul

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Keywords: Sensor, Particulate Matter, Istanbul

Abstract

Istanbul is a metropolitan area with a population of 15 million and a surface area of 1592 km². The air quality of Istanbul has been followed with Air Quality Measurement Stations (AQMS) by Ministry of Environment and Urbanism and Istanbul Metropolitan Municipality for many years. According to The European Union Negotiation, Turkey has to provide the national PM10 daily limit value of 50 µg/m³ in 2019. On the other hand, the average concentration of PM10 is high in Istanbul atmosphere and it is difficult to reach this value in 2019. PM2.5 is not a parameter that defines national limit value yet. It is important that the PM10 and PM2.5 parameters are continuously monitored at multiple points to determine their sources. Sensor technology has been emphasized to follow air pollution and source analysis in many places in recent years and its availability is scientifically discussed. In this study, it was shown that the pollution of Particulate matter can be followed firstly in Istanbul using sensor technique.

1. Introduction

There is a need for more data about dispersion of pollutants and the temporal variation in order to more detail understand processes in the atmosphere. Although Air Quality Monitoring Stations are established in cities and perform reliable measurements, the data received from these stations are not sufficient to determine the spatial and temporal resolution of pollutants. In addition, because operating and establishing of stations is high cost, number of stations is limited. However, 31 air quality stations are trying to determine the air quality all of Istanbul in the current conditions. PM10 parameters are followed in all stations of AQMS, but PM2.5 measurements are made only 4 stations since 2013.

2. Materials and Methods

Particle Material Sensors were placed in the continuous air quality measurement station located at the Avcılar Campus of Istanbul University and simultaneous measurements were made with the AQMS Beta gauge technique. PM10 and PM2.5 data of AQMS were downloaded on online system (www.havaizleme.gov.tr). Sensor module measurement results are downloaded online interface made by the study team.
3. Results

Measurements were made between February 2018 and April 2018. The PM$_{10}$ and PM$_{2.5}$ measurements of sensor showed that a significant correlation with the AQMS measurements for PM$_{10}$ and PM$_{2.5}$ (Figure 1). This study showed that the temporal and spatial variation of the particulate matter can be successfully accomplished using costly sensors in many places in Istanbul.

![Figure 1. Comparison of sensor and AQMS PM$_{10}$ and PM$_{2.5}$ concentrations (µg/m$^3$).](image)

Acknowledgement: Sensor installation, setup and data transfer for establishment of interface were made by PCS Electronics Limited.
Determination of Volatile Organic Compounds in an Adhesive Tape Production Factory Workplace Air.

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Keywords: VOC, indoor air

Abstract

In this study VOC (Volatile Organic Components) levels of indoor air quality of an adhesive tape production facility were investigated. For this purpose, VOC samples were taken in certain places. The samples were examined by GC-MS and VOC species and concentrations were determined.

1. Introduction

In the workplace environments, not exceeding the regulation limit values within the context of Occupational Health and Safety may not always be sufficient to protect employee health. Working with more than one solvent and having various non-solvent chemicals in the workplace environments can cause the worker to be more affected.

2. Materials and Methods

Within the scope of this study, the levels of VOC (Volatile Organic Compounds) in indoor air quality of the adhesive tape production facilities that are operating in Istanbul were investigated. To that end the production unit of the facility with highest VOC level was singled out and, having run two different ventilating systems, VOC types and changes in concentration at different spots were determined by performing measurements.

3. Results

Throughout the study, 40 compounds were detected in 35 VOC samples taken from the indoor environment. The value range of toluene from the detected VOC samples was from 22.8 to 5560 μg/m³, ethylbenzene was from 0.1 to 23.2 μg/m³, xylene was from 2.8 to 197.5 μg/m³ and the value range of benzene was from 0.1 to 1.4 μg/m³. The data acquired from the performed measurements are substantially below the limiting values defined by the occupational health and safety standards. Though, taking in consideration the daily office hours and long years of exposure to these concentrations, it is not likely not to have health issues for workers in long term. General medical examinations must be carried out regularly and, blood tests and urinalysis must be examined cautiously. In addition, effective and efficient operation of the workplace ventilation systems and the feasibility of the designed ventilation systems must be well evaluated. When the ventilation is done with completely outside air, the outdoor air quality is a very important factor and may cause accumulation in the indoor environment.
Cadmium Removal Using Potato Peels as Adsorbent; Kinetic Studies

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Keywords: Adsorption, Cadmium, Potato peels, Kinetics, Isotherms

Abstract

Many pollutant sources, such as industrialization, transportation, uncontrolled waste storage, lead to the accumulation of heavy metals in plants, animals and human beings (Ociepa-Kubicka and Ociepa 2012, Borowiak et al. 2016). Cadmium (Cd), which is one of the heavy metals, can be found in the structure of the soil, water, sediment as well as industrial activities, such as phosphorus fertilizers, sewage wastes or atmospheric transport (Assche and Clijsters 1990). According to the World Health Organization (WHO), tolerable cadmium uptake 25 μg /per kg of body weight for the food and to be 3 μg / l in drinking water was accepted (WHO 2010). When exposed to high cadmium in humans; kidney, lung, and prostate cancers have been observed (Özbek et al. 1995) but have been reported in effects such as bone erosion, anemia, tooth decay, and loss of sense of smell. Adsorption process; it is an appropriate treatment method when compared with other methods in terms of easiness and efficacy in wastewater treatment (Anastopoulos and Kyzas 2014). In these studies many materials such as; waste sludge (Chen and Wang 2008), potato peels (Kyzas et al.2016), olive kernel (Kula et al. 2008), nanoparticles (Elkhatib et al. 2016), Laminaria japonica (Ghimire et al. 2008), brown-red-green algae (Hashim and Chu 2004), Aspergillus niger (Mungasavalli et al. 2007), Neurospora crassa (Tunali et al. 2005), Mucor hiemalis (Tewari et al 2005), Botrytis cinerea (Akar et al. 2005), waste algae (Kuncoro et al. 2017) and surface modified bacteria (Tafakori et al. 2017) were used as adsorbents. Despite the fact that adsorption with activated carbon is very effective in removing pollutants in the solutions, the high production cost makes it not economical to use in the adsorption process. Therefore, low cost adsorbents are being tried to be developed as an alternative to activated carbon (Yuzhu and Viraraghavan 2002, Hoseinzadeh et al. 2014). In this study; potato shell, a waste-natural material, was used as a cheap-cost adsorbent, cadmium removal efficiency and adsorption characteristics were investigated. In this study, untreated waste potato shells were used as adsorbents and cadmium removal mechanisms were investigated. Maximum removal efficiency; at pH 5.8 at room temperature, 92% at initial concentration of 100 mg
/ 1 Cd$^{2+}$ and 4.6 mg of cadmium removed per gram of adsorbent. However, the higher cadmium initial concentrations increased by 91% and the cadmium recovered per adsorbent rose to 22.8 mg /g. Under optimum conditions; two parameter equilibrium isotherms (Langmuir, Freundlich, Temkin etc.) were applied. Freundlich isotermin has the highest correlation (99.9%) in isotherms. Isothermal adsorption capacity ($K_F$): 19.94 mg /g and heterogeneity factor ($1/n$) 1.0 was determined. In adsorption, it was found that both the boundary layer diffusion and the intra-particle diffusion steps were effective, and the determination of the adsorption rate showed that the Type I Pseudo Second Order Equation had a high correlation (99%) at all concentrations.

References


# Authors Index

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adar E. 199</td>
<td>Babayiğit E. 15</td>
</tr>
<tr>
<td>Adıgüzel E. 228</td>
<td>Bağcılar E. 11</td>
</tr>
<tr>
<td>Adiller A. 199</td>
<td>Bakaraki-Turan N. 44</td>
</tr>
<tr>
<td>Ağbulut N. 127, 130, 272</td>
<td>Balçık B. 220</td>
</tr>
<tr>
<td>Ahmetli G. 109, 262</td>
<td>Balkaya M. 287, 290, 292</td>
</tr>
<tr>
<td>Aku Ö. 183, 305</td>
<td>Balkaya N. 288, 291, 294, 300, 301</td>
</tr>
<tr>
<td>Akmehtem Balcıoğlu I. 151</td>
<td>Barut F. 58</td>
</tr>
<tr>
<td>Aksit Sahinkaya S. 119</td>
<td>Bas B. 42</td>
</tr>
<tr>
<td>Akyurt S. 187</td>
<td>Başli B. 234</td>
</tr>
<tr>
<td>Al O. 302</td>
<td>Baylan N. 242, 244, 246, 248</td>
</tr>
<tr>
<td>Alagöz B.A. 154</td>
<td>Bayrakdar A. 23</td>
</tr>
<tr>
<td>Allwar A. 39</td>
<td>Bektaş N. 51</td>
</tr>
<tr>
<td>Al-Mallah J. 72</td>
<td>Beler-Baykal B. 76, 117</td>
</tr>
<tr>
<td>Alpar G. 300</td>
<td>Benredouane S. 254, 258</td>
</tr>
<tr>
<td>Alper D. 15</td>
<td>Beriber A. 254</td>
</tr>
<tr>
<td>Altınbasa M. 76</td>
<td>Berrama T. 254, 258</td>
</tr>
<tr>
<td>Alver Şahin Ü. 183, 185, 303, 305</td>
<td>Bertanza G. 101</td>
</tr>
<tr>
<td>Alviansah T. 39</td>
<td>Billy E. 92</td>
</tr>
<tr>
<td>Amanda V. 279</td>
<td>Bollati E. 101</td>
</tr>
<tr>
<td>Apaydın Ö. 207</td>
<td>Bonçukcuoğlu R. 302</td>
</tr>
<tr>
<td>Apaydın Ö. 171</td>
<td>Bouhidél K.E. 19, 78</td>
</tr>
<tr>
<td>Arabacı A. 275</td>
<td>Burak S. 122</td>
</tr>
<tr>
<td>Arslan Alaton I. 9</td>
<td>Büyükakacı N. 11</td>
</tr>
<tr>
<td>Arslan-Alaton I. 205</td>
<td>C</td>
</tr>
<tr>
<td>Atav R. 60</td>
<td>Cakırgöz M. 72</td>
</tr>
<tr>
<td>Ateş A.E. 298</td>
<td>Calgan E. 94</td>
</tr>
<tr>
<td>Ateş A.E. 171, 174</td>
<td>Camcıoğlu Ş. 80, 82, 85, 260</td>
</tr>
<tr>
<td>Ateş Ç. 80</td>
<td>Cavallotti I. 101</td>
</tr>
<tr>
<td>Ateş S. 298</td>
<td>Cavkas S. 117</td>
</tr>
<tr>
<td>Avcı A. 248</td>
<td>Celebi M. 270</td>
</tr>
<tr>
<td>Awayes J. 117</td>
<td>Celik E. 5</td>
</tr>
<tr>
<td>Ayachi A. 209</td>
<td>Chen W. 30</td>
</tr>
<tr>
<td>Aydin M.I. 167</td>
<td>Chung G.B. 88</td>
</tr>
<tr>
<td>Aydin S. 167, 232, 267</td>
<td>Ciftcioglu B. 47</td>
</tr>
<tr>
<td>Aydin I. 173</td>
<td>Citrawedi P.W. 216</td>
</tr>
<tr>
<td>Aydin M.I. 171, 174</td>
<td>Cobanoglu Kayikci C.B. 296</td>
</tr>
<tr>
<td>Aydin S. 230, 234</td>
<td>Cogor E. 47</td>
</tr>
<tr>
<td>Ayol A. 146, 147</td>
<td>Cosgun S. 68</td>
</tr>
<tr>
<td>Aysal N. 294</td>
<td>Coudray M. 92</td>
</tr>
<tr>
<td>Ayvaz C. 183, 185, 303, 305</td>
<td>Cumbul Altay M. 56</td>
</tr>
<tr>
<td>Azmi U. 34</td>
<td>Çalhan R. 148</td>
</tr>
</tbody>
</table>

310
<table>
<thead>
<tr>
<th>Author Name</th>
<th>Page Numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Çalışkan Y.</td>
<td>51</td>
</tr>
<tr>
<td>Çallı B.</td>
<td>13, 120</td>
</tr>
<tr>
<td>Çallı B.</td>
<td>72</td>
</tr>
<tr>
<td>Çatalbaş A.</td>
<td>224</td>
</tr>
<tr>
<td>Çelebi E.E.</td>
<td>51</td>
</tr>
<tr>
<td>Çelik G.</td>
<td>151</td>
</tr>
<tr>
<td>Çelikkol I.</td>
<td>303</td>
</tr>
<tr>
<td>Çetinkaya Ateşi Z.</td>
<td>250</td>
</tr>
<tr>
<td>Çifçi D.I.</td>
<td>60</td>
</tr>
<tr>
<td>Çiner F.</td>
<td>148</td>
</tr>
<tr>
<td>Dadou S.</td>
<td>254, 258</td>
</tr>
<tr>
<td>Darma D.D.</td>
<td>64</td>
</tr>
<tr>
<td>Demet B.</td>
<td>70</td>
</tr>
<tr>
<td>Demir A.</td>
<td>199</td>
</tr>
<tr>
<td>Demirkaya E.</td>
<td>47</td>
</tr>
<tr>
<td>Deniz S.</td>
<td>32</td>
</tr>
<tr>
<td>Denktaş C.</td>
<td>70</td>
</tr>
<tr>
<td>Desiyani E.</td>
<td>218</td>
</tr>
<tr>
<td>Deveci F.</td>
<td>264</td>
</tr>
<tr>
<td>Dinc G.</td>
<td>104</td>
</tr>
<tr>
<td>Dincer I.</td>
<td>159, 180, 189</td>
</tr>
<tr>
<td>Dincer K.</td>
<td>2</td>
</tr>
<tr>
<td>Dindaş G.B.</td>
<td>51</td>
</tr>
<tr>
<td>Dogruyol P.</td>
<td>288, 291</td>
</tr>
<tr>
<td>Doğan M.</td>
<td>303</td>
</tr>
<tr>
<td>Doufene N.</td>
<td>258</td>
</tr>
<tr>
<td>Dufaud V.</td>
<td>92</td>
</tr>
<tr>
<td>Dumanoğlu Y.</td>
<td>185, 305</td>
</tr>
<tr>
<td>Düzen H.</td>
<td>28</td>
</tr>
<tr>
<td>Efe M.</td>
<td>303</td>
</tr>
<tr>
<td>Ekmekeyapar F.</td>
<td>187</td>
</tr>
<tr>
<td>Elginoz N.</td>
<td>42, 103</td>
</tr>
<tr>
<td>Elmaslar Özbaş E.</td>
<td>220, 222, 224, 226, 228, 230, 232, 234</td>
</tr>
<tr>
<td>Emik S.</td>
<td>267</td>
</tr>
<tr>
<td>Engiz G.</td>
<td>156</td>
</tr>
<tr>
<td>Erdem İ.C.</td>
<td>13</td>
</tr>
<tr>
<td>Erdinçler A.</td>
<td>15, 124, 154</td>
</tr>
<tr>
<td>Ergun E.</td>
<td>130</td>
</tr>
<tr>
<td>Ergüç M.</td>
<td>49, 62, 236, 238</td>
</tr>
<tr>
<td>Erkan E.</td>
<td>301</td>
</tr>
<tr>
<td>Erman İ.</td>
<td>39</td>
</tr>
<tr>
<td>Eroğlu S.</td>
<td>56</td>
</tr>
<tr>
<td>Faisala M.</td>
<td>21</td>
</tr>
<tr>
<td>Fariduddin S.</td>
<td>64</td>
</tr>
<tr>
<td>Fatimah I.</td>
<td>34, 216, 218</td>
</tr>
<tr>
<td>Ferreri M.</td>
<td>101</td>
</tr>
<tr>
<td>Fersiz S.</td>
<td>41</td>
</tr>
<tr>
<td>Furtun M.</td>
<td>80, 260</td>
</tr>
<tr>
<td>Gania A.</td>
<td>21</td>
</tr>
<tr>
<td>Genisoglu M.</td>
<td>175</td>
</tr>
<tr>
<td>Germirli Babuna F.</td>
<td>42, 103, 119</td>
</tr>
<tr>
<td>Gkiouzepas S.</td>
<td>17</td>
</tr>
<tr>
<td>Goktas H.M.</td>
<td>156</td>
</tr>
<tr>
<td>Goren A.Y.</td>
<td>175</td>
</tr>
<tr>
<td>Gunes Y.</td>
<td>58</td>
</tr>
<tr>
<td>Guneysu S.</td>
<td>302</td>
</tr>
<tr>
<td>Guvenc S.Y.</td>
<td>2, 199, 202</td>
</tr>
<tr>
<td>Güneş E.</td>
<td>60</td>
</tr>
<tr>
<td>Güneş Y.</td>
<td>60</td>
</tr>
<tr>
<td>Güneyusu S.</td>
<td>230, 232</td>
</tr>
<tr>
<td>Güven Oral E.</td>
<td>74</td>
</tr>
<tr>
<td>Gwak G.</td>
<td>90</td>
</tr>
<tr>
<td>Halilibrahimoğlu N.</td>
<td>246</td>
</tr>
<tr>
<td>Hapoğlu H.</td>
<td>80, 82, 85, 260</td>
</tr>
<tr>
<td>Harjati F.</td>
<td>218</td>
</tr>
<tr>
<td>Haumesser P.H.</td>
<td>92</td>
</tr>
<tr>
<td>Hidayah A.R.M.</td>
<td>64</td>
</tr>
<tr>
<td>Hidayat H.</td>
<td>279</td>
</tr>
<tr>
<td>Hoşgün S.</td>
<td>24</td>
</tr>
<tr>
<td>Hsu L.</td>
<td>30</td>
</tr>
<tr>
<td>Iatsunskyi I.</td>
<td>7</td>
</tr>
<tr>
<td>Ilgaz Y.B.</td>
<td>32</td>
</tr>
<tr>
<td>İnan H.</td>
<td>264, 277</td>
</tr>
<tr>
<td>İlkılıç N.E.</td>
<td>305</td>
</tr>
<tr>
<td>İnan H.</td>
<td>112, 250</td>
</tr>
<tr>
<td>İnce E.</td>
<td>127, 130, 272</td>
</tr>
<tr>
<td>İnce M.</td>
<td>127, 130, 272</td>
</tr>
<tr>
<td>İnci İ.</td>
<td>246, 248</td>
</tr>
<tr>
<td>Javani N.</td>
<td>191</td>
</tr>
<tr>
<td>Ju H.</td>
<td>90</td>
</tr>
<tr>
<td>Kajjumba G.W.</td>
<td>267</td>
</tr>
<tr>
<td>Kalin R.M.</td>
<td>17</td>
</tr>
<tr>
<td>Kan M.Y.</td>
<td>88</td>
</tr>
<tr>
<td>Kantoğlu Ö.</td>
<td>130</td>
</tr>
</tbody>
</table>
Abstract Book of the 4rd International Conference on Recycling and Reuse
October 24-26, 2018 - Istanbul / TÜRKİYE

312

Karaagac B. 96
Karabağ N. 132, 136
Karabey P. 236
Karacal P.N. 103
Karanfil F. 49
Karaoğlu A.G. 125
Karaş P. 43
Kaya Özsel B. 58
Keleş B. 226
Kerimak Öner M.N. 41
Khataee A. 144
Khoirunnisa 216
Kırkayak Ö. 130
Kiviclemdan Moral Ç. 99
Knapp Charles W. 17
Kobya M. 66, 144
Koca A. 277
Kocdag E. 171
Kodaman C.G. 238
Komıya T. 252
Korkmaz G. 234
Kulak N. 232
Kunarti E.S. 36
Kunt B. 68
Kurtoglu Akkaya G. 142

L
Lai C.J. 88
Lee C.Y. 88

M
Martienssen M. 140
Matsuda F. 53
Maulama A.P. 64
Mavzer E. 228
Mendil-Jakani H. 92
Merniz I. 209
Mert E. 230
Miyake M. 252
Muhammetoglu A. 114
Muhammetoglu H. 114
Mulanaa F. 21
Musawwa M.M. 36

N
Nag M. 26
Najah F.B. 34
Nemlioglu S. 295, 296

Ö
Ölmez Hanci T. 9
Özcan H.K. 220, 222, 226, 228, 230, 232
Özdemir M. 24
Özer A. 45, 49, 62, 236, 238
Özkan E. 207
Özkaraova E.B. 17, 74
Özkaya B. 70
Özkaya F. 183
Özön E. 124
Öztürk D. 43
Özyurt B. 80, 82, 85, 260

P
Palabiyik B.B. 282, 306
Pala-Ozkok I. 47
Pavlenko M. 7
Pedrazzani R. 101
Pehlivan Ö. 9
Prakoso N.I. 53
<table>
<thead>
<tr>
<th>Name</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Putra R.S.</td>
<td>64</td>
</tr>
<tr>
<td>Q</td>
<td></td>
</tr>
<tr>
<td>Quezada G.R.</td>
<td>164</td>
</tr>
<tr>
<td>R</td>
<td></td>
</tr>
<tr>
<td>Rapti A.T.</td>
<td>173</td>
</tr>
<tr>
<td>Reçber N.</td>
<td>194</td>
</tr>
<tr>
<td>Rozas R.E.</td>
<td>164</td>
</tr>
<tr>
<td>Rubiyanto D.</td>
<td>34</td>
</tr>
<tr>
<td>S</td>
<td></td>
</tr>
<tr>
<td>Sadeghi Rad T.</td>
<td>144</td>
</tr>
<tr>
<td>Saffarzadeh A.</td>
<td>26</td>
</tr>
<tr>
<td>Saffarzadeh A.</td>
<td>252</td>
</tr>
<tr>
<td>Safi S.</td>
<td>106</td>
</tr>
<tr>
<td>Sahmurova A.</td>
<td>294,300</td>
</tr>
<tr>
<td>Salt Y.</td>
<td>70</td>
</tr>
<tr>
<td>Santini C.</td>
<td>92</td>
</tr>
<tr>
<td>Sarabi S.M.</td>
<td>66</td>
</tr>
<tr>
<td>Sargil T.</td>
<td>85</td>
</tr>
<tr>
<td>Sarialtin V.</td>
<td>96</td>
</tr>
<tr>
<td>Sari-Erkan H.</td>
<td>44</td>
</tr>
<tr>
<td>Seker B.</td>
<td>114</td>
</tr>
<tr>
<td>Selcuk H.</td>
<td>167,171,173,174,179</td>
</tr>
<tr>
<td>Selçuk H.</td>
<td>148,306</td>
</tr>
<tr>
<td>Semerçi N.</td>
<td>68,120</td>
</tr>
<tr>
<td>Sener M.</td>
<td>288,291</td>
</tr>
<tr>
<td>Senoussi H.</td>
<td>19</td>
</tr>
<tr>
<td>Sert R.</td>
<td>205</td>
</tr>
<tr>
<td>Setiawan A.</td>
<td>39</td>
</tr>
<tr>
<td>Seyitoğlu S.S.</td>
<td>136</td>
</tr>
<tr>
<td>Sezgin N.</td>
<td>294,295,297</td>
</tr>
<tr>
<td>Sezgin P.</td>
<td>300</td>
</tr>
<tr>
<td>Shimaoaka T.</td>
<td>26,252</td>
</tr>
<tr>
<td>Sim Y.</td>
<td>34</td>
</tr>
<tr>
<td>Siuzdak K.</td>
<td>7</td>
</tr>
<tr>
<td>Sofuoğlu A.</td>
<td>175</td>
</tr>
<tr>
<td>Sogancioglu M.</td>
<td>96,109,262</td>
</tr>
<tr>
<td>Soğancioglu M.</td>
<td>106</td>
</tr>
<tr>
<td>Su E.</td>
<td>156</td>
</tr>
<tr>
<td>Sutarno</td>
<td>36</td>
</tr>
<tr>
<td>Sürmeli R.Ö.</td>
<td>72</td>
</tr>
<tr>
<td>Süzen Y.</td>
<td>240</td>
</tr>
<tr>
<td>Ş</td>
<td></td>
</tr>
<tr>
<td>Şengül H.</td>
<td>194</td>
</tr>
<tr>
<td>Şengül S.</td>
<td>82</td>
</tr>
<tr>
<td>T</td>
<td></td>
</tr>
<tr>
<td>Taher M.N.</td>
<td>76,117</td>
</tr>
<tr>
<td>Taushiyah A.</td>
<td>34</td>
</tr>
<tr>
<td>Tekbaş M.</td>
<td>51</td>
</tr>
<tr>
<td>Temelli U.E.</td>
<td>295</td>
</tr>
<tr>
<td>Temiz M.</td>
<td>191</td>
</tr>
<tr>
<td>Tezer Yurdakoş Ö.</td>
<td>146,147</td>
</tr>
<tr>
<td>Toledo P.G.</td>
<td>164</td>
</tr>
<tr>
<td>Toprak F.</td>
<td>49</td>
</tr>
<tr>
<td>Topuz E.</td>
<td>226</td>
</tr>
<tr>
<td>Turan A.</td>
<td>127,130,272</td>
</tr>
<tr>
<td>U</td>
<td></td>
</tr>
<tr>
<td>Ulker D.</td>
<td>122</td>
</tr>
<tr>
<td>Umazawa T.</td>
<td>53</td>
</tr>
<tr>
<td>Unver H.</td>
<td>47</td>
</tr>
<tr>
<td>Uslu Y.A.</td>
<td>127,130,272</td>
</tr>
<tr>
<td>Uysal A.</td>
<td>5</td>
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<tr>
<td>Uzun B.</td>
<td>183,185,303,305</td>
</tr>
<tr>
<td>Uzunoğlu D.</td>
<td>45,49,236,238</td>
</tr>
<tr>
<td>Ü</td>
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<tr>
<td>Varank G.</td>
<td>2,199,202</td>
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<td>Wardani R.M.I.</td>
<td>64</td>
</tr>
<tr>
<td>Y</td>
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<td>Yeh C.C.</td>
<td>88</td>
</tr>
<tr>
<td>Yel E.</td>
<td>104,106,109,262,270</td>
</tr>
<tr>
<td>Yenigün O.</td>
<td>154</td>
</tr>
<tr>
<td>Yildiz M.</td>
<td>99</td>
</tr>
<tr>
<td>Yigit Hunce S.</td>
<td>234</td>
</tr>
<tr>
<td>Yıldırım E.</td>
<td>267</td>
</tr>
<tr>
<td>Yu J.W.</td>
<td>88</td>
</tr>
<tr>
<td>Yun S.</td>
<td>90</td>
</tr>
<tr>
<td>Yüzer B.</td>
<td>167,173,174,189</td>
</tr>
<tr>
<td>Yüksel E.</td>
<td>127</td>
</tr>
<tr>
<td>Yüzer B.</td>
<td>148</td>
</tr>
<tr>
<td>Z</td>
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</tr>
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<td>Zamouche M.</td>
<td>209</td>
</tr>
<tr>
<td>Zekkaoui C.</td>
<td>254,258</td>
</tr>
<tr>
<td>Zengin G.E.</td>
<td>47</td>
</tr>
<tr>
<td>Ziliani E.</td>
<td>101</td>
</tr>
</tbody>
</table>