RECYCLING AND REUSE, 2016

3rd INTERNATIONAL CONFERENCE ON RECYCLING AND REUSE

FULL TEXT PROCEEDINGS

Editors
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Namik Kemal University Environmental Engineering Department


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PREFACE

International Conference on Recycling and Reuse (R&R, 2016) organized by two leading universities of Türkiye; Istanbul University and Namik Kemal University, was held in Istanbul, 28-30 September, 2016. 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 250 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, 2016 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, 2016 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, Water Science and Technology, Water Science and Technology: Water Supply, Water Practice and Technology which provided special efforts to publish the selected conference papers. Finally, we thank all participants without whom the R&R, 2016 Conference would not have been possible.

We would like to welcome you at the forthcoming 4th International Conference on Recycling and Reuse (R&R, 2018).

September 2016, Istanbul

Prof. Dr. Hüseyin Selçuk
Prof. Dr. Süreyya Meriç
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<table>
<thead>
<tr>
<th>Name</th>
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Ozonation for the Removal of Bisphenol-A from Aqueous Solutions

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Keywords: Degradation kinetics, by-product formation, pH effect, ozonation, Bisphenol A.

Abstract

100 mg.L⁻¹ Bisphenol A (BPA) containing synthetic water samples have been exposed to ozone process for 90 minutes. Three different pH conditions (pH 3, 7 and 10) were tested to achieve an effective treatment of BPA by monitoring the concentration and mineralization simultaneously. 5.3 mg.min⁻¹ gaseous ozone was supplied into the aqueous solution of BPA where its removal was best fitted to pseudo-first order kinetics. Alkaline conditions promoted the fastest removal showing the highest observed reaction rate constant which was calculated as 0.15 min⁻¹. Under optimum conditions (pH 10) 30 minutes satisfied the complete removal of BPA however, 40% mineralization was achieved after 90 minutes and remain constant. Commonly ring structured byproducts were observed under pH 3 and 7 conditions indicating the lower degree of mineralization.

1. Introduction

Bisphenol A (BPA) is produced over 2.7 billion kilogram worldwide every year (Vandenberg et al, 2007). 99.9 % of BPA that is produced is used for the production of polycarbonate plastic, epoxy resin and other plastic products (Staples et al, 1998). It is consumed in a wide range of products for different purposes that include; optical lenses, thermal paper, protective coating, automotive lenses, electrical parts, building materials, compact disks, and flame retardants and in the linings inside of cans (Staples et al. 1998).

BPA is released into the environment during its manufacture, handling and transportation as dust and other emissions, inefficiently treated industrial wastewaters and leaching through the landfill applications of the solid wastes (Staples et al, 1998). BPA is listed in Directive 2013/39/EU as a priority compound that affects aquatic ecosystems (Ribeiro, A.R. et al, 2015). The greatest concern about BPA in the environment is that it has been identified as an Endocrine Disrupting Chemical (EDC) more specifically a xenoestrogen, which is a class of chemicals that interfere with the natural operation of Estradiol and other endogenous estrogens (Wozniak et al. 2005). Endocrine disruptive chemicals interrupts the natural behavior of endocrine system and cause malfunctions.

BPA molecule is made up of two phenol moieties that are attached to an acetone molecule (Figure 1). Treatment of BPA is difficult by conventional wastewater treatment methods because of its physico-chemical properties (Table 1) mainly that having a stable ring structure, low solubility in water and low vapor pressure.
Table 1. Physicochemical properties of Bisphenol-A (EPA, 2012)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Molecular Formula</td>
<td>C₁₅H₁₆O₂</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>228.29</td>
</tr>
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<td>Water solubility (20-25°C)</td>
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<tr>
<td>Log $K_{ow}$ (25°C)</td>
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<td>Henry’s law constant</td>
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<td>Melting point</td>
<td>153°C</td>
</tr>
<tr>
<td>Boiling point (4mmHg)</td>
<td>220°C</td>
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<tr>
<td>Vapour pressure</td>
<td>5x10⁻⁶ Pa</td>
</tr>
<tr>
<td>EC₅₀ green algae (96h)</td>
<td>1.389</td>
</tr>
</tbody>
</table>

Figure 1. Bisphenol-A molecular structure

Advanced oxidation processes (AOPs) regarded as the best treatment method in order to eliminate such recalcitrant organic chemicals from water bodies. Among all, ozonation process has been efficiently used to oxidize even the toughest recalcitrant species in water. In addition, ozonation has the advantages of being very rapid in its action and does not require any addition of chemicals. The aim of this study is to investigate degradation kinetics and mineralization of BPA and monitor the formation of by-products under low dose application to mimic the real wastewater treatment conditions.

2. Material Methods

2.1 Materials
Bisphenol A (97% purity, for synthesis), Ortho-Phosphoric acid (85%, GR for analysis), sodium thiosulphate (97%, anhydrous), potassium iodide (Emprove* api, suitable for use as an active pharmaceutical ingredient), sodium chloride (99.5%, for analysis), sodium sulfate (99.0-100.5%, anhydrous suitable for use as excipient), sodium dihydrogen phosphate monohydrate (98.0-100.5%, suitable for use as an excipient), sulphuric acid (98%, reagent grade), dichloromethane (99.9%, for liquid chromatography), acetic acid (glacial, 100%, anhydrous for analysis), acetonitrile (99.9%, gradient grade for liquid chromatography), sodium carbonate (anhydrous), sodium hydrogen carbonate and potassium hydrogen phthalate were all products of Merck Milipore, Germany and were supplied by Tin Chemical and Laboratory Supplies and Devices, Turkey. Sodium hydroxide (98-100%, pellets, analytical grade) and hydrochloric acid (36.5-38%, analytical grade), potassium indigo trisulfonate (ozone scavenging reagent) and starch (reagent grade) were products of Sigma-Aldrich chemicals and purchased from Tin Chemical and Laboratory Supplies and Devices, Turkey.
2.2 Experimental Setup
Ozonation experiments were conducted with 100 mg.L-1 aqueous BPA solutions in an Erlenmeyer flask having 2 liter capacity. Gaseous ozone was supplied by a bench type ozone generator with a rate of 5.3 mg.min-1. Reactor was placed on a stirrer for mixing. pH of the solution was measured and adjusted throughout the experiment by addition of hydrochloric acid and sodium hydroxide solutions. 15 ml samples were collected during ozonation experiment at 0, 1, 3, 5, 7, 10, 25, 45, 60 and 90 minutes for concentration (HPLC) and mineralization (TOC) analyses. Experimental setup is shown in Figure 2.

![Figure 2. Experimental setup of ozonation of BPA](image)

2.3 Analysis Methods
Gaseous ozone concentration has been measured by potassium iodide method (Erol, F. 2008) and dissolved ozone concentration was determined by indigo colorimetric methods (APHA, AWWA, WEF, 2005) in 1000 ml of aqueous solutions. BPA concentration measurements were conducted by High Performance Liquid Chromatography (mobile phase: 60% water, 40% acetonitrile with 1 ml/min flowrate, column: GL sciences Inertsil ODS-4, injection volume: 100 µL, detector: UV-278nm) and mineralization by Total Organic Carbon Analyzer (TOC). By-product determination was conducted by Gas Chromatography Mass Spectrometer (GC-MS). Evaluation of the data was conducted by the help of NIST approved Wiley library.

3. Results and Discussion
This study mainly focused on understanding BPA removal and oxidation mechanism during ozonation of solutions containing BPA at different pH values. In order to investigate
degradation mechanism HPLC and TOC analyses were conducted as the first thing then side products in the solution were investigated by using GC-MS.

BPA removal at different pH values were compared by fitting the concentration data in to pseudo first order reaction kinetics. These data are presented in Figure 3a along with TOC removal data presented in Figure 3b.

The degradation of BPA at pH 10 was faster than pH 7 and was more complete than at pH 3. This has been reported in literature as well, and is due to the greater concentration of hydroxyl radicals as compared to O₃ molecules at higher pH values. Hydroxyl radicals have greater oxidation potential than O₃ molecules and therefore will degrade BPA faster and more efficiently than O₃.

In terms of TOC removal, pH3 and pH7 are rather similar in that they both achieved 10% removal of TOC after 90 minutes however the removal of TOC at pH7 was mostly during the first 30 minutes, while that of pH3 peaked after 30 minutes. pH 10 had a significantly higher TOC removal percentage with a maximum of 40% TOC removed.

Differences between these runs also give some idea about reaction mechanism; when all three analyses combined together it can be observed that decrease in BPA concentration, TOC removal and emergence of side product peaks (HPLC chromatograms) are related. TOC removal increase is observed as BPA concentration is decreased and side product peaks emerges. It can be observed from Figure 4 (similar trend can also be observed from Figure 5) that side product peaks emerges at 25 minutes while TOC removal starts to increase and BPA concentration in the medium is 80 mg.L⁻¹. This may suggest that during the degradation of BPA some side products are formed and a part of them can be mineralized (oxidized in to CO₂ and water).

**Figure 3.** 100 mg.L⁻¹ Bisphenol-a degradation curves (a) and mineralization (b) under various pH conditions.
The relationship between BPA degradation, side product formation (the ones that can be detected by HPLC method for detection of BPA) and TOC removal can be observed from figures 3 and 4. Degradation of BPA is results some byproducts and oxidation of these species is conducted along with BPA and mineralization starts along with emergence of other species in chromatograms. It is difficult to observe this pattern in chromatograms obtained from the samples taken at pH 10. This might resulted from faster degradation of BPA and having different oxidation species in the medium (ozone is dominant in acidic conditions while hydroxyl radicals are dominant in basic conditions). It is not easy to determine these species with HPLC-UV analysis although the side products which were appeared in chromatograms obtained at pH 3 and 7 were not observed in chromatograms obtained from the runs conducted at pH 10. Increase in TOC removal in the runs conducted at pH 10 might be attributed to oxidation of these species with hydroxyl radicals.

GCMS chromatograms of the treated BPA solutions are given in Figure 6. Namely identified byproducts are as follows: Benzoic acid, 4-hydroxy (pH 3), 2-Phenylbenzquinone (pH 3), 4-Octen-3-one (pH 3), Dipropyl phthalate (pH 7), 2-Isononenal (pH 7), Cyclohexane,1-[2-(4-ethylcyclohexyl)ethyl]-4-pentyl (pH 7), Hexadecanoic acid, methyl ester (pH 7 and pH 10).
Figure 6. GCMS chromatograms of ozonated Bisphenol-A solutions under various pH

References

Continuous versus Batch Contacting for Nutrient Recovery from Human Urine upon Processing with Clinoptilolite I: Surface Capacities and Operation Times

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Keywords: Nutrient recovery, human urine, fertilizer, clinoptilolite, ion exchange/adsorption, batch and continuous modes.

Abstract

Ion exchange/adsorption with clinoptilolite from human urine is one proven method for nutrient recovery from source separated human urine. Although this method can be applied in either batch or continuous mode, almost all work in the literature was focused on the batch mode. The aim of this work was to determine and to compare surface capacities and operation times for both of these two modes to identify the more effective one for nutrient recovery under similar conditions. Using initial ammonium loadings between 10-40 mg ammonium/g clinoptilolite for the batch mode and empty bed contact times between 30-120 minutes for the continuous mode, it was observed that higher surface capacities and lower operation times were achieved in the continuous mode while higher efficiencies and lower residual concentrations were observed for the batch mode. From the standpoint of surface capacities and operation times, continuous mode seems preferable over batch operation for nutrient recovery from human urine with clinoptilolite through ion exchange/adsorption.

1. Introduction

A recent approach to domestic wastewater management is stream segregation at the source which enables the reuse of each fraction, and therefore helps sustainability of resources. One of those streams, yellow water is human urine, which is a renewable and recyclable material. Its rich nutrient content in terms of nitrogen, phosphorus and potassium makes it a valuable alternative source of fertilizers through either direct or indirect use. Processing it with the natural zeolite clinoptilolite is an effective method of recovering plant nutrients for further use as fertilizer (Lind et al., 2000; Beler Baykal et al., 2004; 2009; 2011; Ganrot et al., 2007; 2008; Kocaturk and Beler Baykal, 2012; Allar and Beler Baykal, 2013; 2015), where nutrients in urine is transferred onto zeolite, subsequently to be made available to plants.

Within that context, human urine is contacted with clinoptilolite to load nutrients onto the zeolite through ion exchange/adsorption to produce nutrient enriched clinoptilolite which can be used as the fertilizer product. After loading, nutrient enriched clinoptilolite is applied onto soil as fertilizer, and nutrients on loaded clinoptilolite are released upon contact with water, either through irrigation or upon precipitation, and are made available for plant growth. The nutrient loading phase of this application can be carried out in two modes as batch or continuous. When human urine is contacted with clinoptilolite with 100% recycle for batch mode, initial ammonium loading is the main parameter (Beler Baykal et al., 2009). For continuous mode, human urine passes through clinoptilolite column continuously and empty bed contact time becomes the main parameter (Droste, 1997).
Majority of the work on this subject matter is focused upon batch-wise operation to load nutrients in urine onto clinoptilolite (Beler Baykal et al., 2004; 2011; Allar and Beler Baykal, 2013). Considering that the expected capacity in a continuous ion exchanger/adsorber should be higher as compared to its batch counterpart due to always being in contact with the highest possible liquid phase concentration, this paper aims to observe the characteristics of system behavior under continuous flow conditions together with the more widely used batch-wise contacting. Specific focus is placed upon breakthrough profiles, surface concentrations/capacities and operation times.

2. Material and Methods

Source separated human urine was stored at least two months after collection. As urea is the most common form of nitrogen in fresh human urine, storage is significant to ensure completion of its hydrolysis to provide the ionic form, $\text{NH}_4^+$, to be removed through ion exchange. pH of stored urine was adjusted to around 7 at the beginning of the loading experiments. Natural clinoptilolite from Gordes (Turkey) was used as ion exchanger/adsorbent with a particle size of 1-2 mm. The clinoptilolite was preconditioned with 1 M NaCl to attain the sodium form for increasing ammonium exchange capacity.

Batch loadings were made in columns of 3.6 cm diameter with 100% recycle for 10-40 mg NH4/g clinoptilolite initial loadings. The flowrate was the same for all loadings as 10 mL/min. Samples were taken from the feed tank in time and compared with the initial concentrations.

Continuous loadings were also carried out in a column with a diameter of 3.6 cm for a range of 30-120 minutes contact times (tc) and samples were taken from the column effluent continuously. Feed concentrations were measured at the beginning and very end of the experiment to observe that no changes have occurred.

The experimental setup is shown in Figure 1 and experimental conditions are given in Table 1 for the batch mode and Table 2 for the continuous mode. All samples were analyzed for ammonium with an Orion ion meter/ammonia probe and orthophosphate with the Stannous Chloride Method of Standard Methods (Standard Methods, 2005).

![Figure 1. The basic experimental setup for batch and continuous mode](image-url)
3. Results and Discussion

This work was made with the primary aim of determining surface capacities and operation times in the batch and continuous modes for nutrient recovery from human urine with clinoptilolite through ion exchange/adsorption. The results are presented in Figures 2 - 3, and Tables 3 - 4.

Table 1. Experimental conditions for batch loadings

<table>
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<th>Initial loading</th>
<th>Bed height</th>
<th>Amount of clinoptilolite</th>
<th>Volume of urine</th>
<th>Initial concentration</th>
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<td>mg NH₄/g clinoptilolite</td>
<td>cm</td>
<td>g</td>
<td>mL</td>
<td>mg NH₄/L</td>
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<td>750.318</td>
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<td>7175</td>
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<td>15</td>
<td>92.2</td>
<td>750.242</td>
<td>1631</td>
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<td>20</td>
<td>98.0</td>
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<td>2003</td>
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<td>25</td>
<td>89.8</td>
<td>750.672</td>
<td>2615</td>
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<td>30</td>
<td>89.0</td>
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<td>40</td>
<td>29.0</td>
<td>202.507</td>
<td>1000</td>
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Table 2. Experimental conditions for continuous loadings

<table>
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<th>Contact time</th>
<th>Bed height</th>
<th>Flowrate</th>
<th>Amount of clinoptilolite</th>
<th>Influent concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>min</td>
<td>cm</td>
<td>mL/min</td>
<td>g</td>
<td>mg NH₄/L</td>
</tr>
<tr>
<td>30</td>
<td>15.3</td>
<td>5.2</td>
<td>100.092</td>
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<td>90</td>
<td>15.9</td>
<td>1.8</td>
<td>100.096</td>
<td>8125</td>
</tr>
<tr>
<td>120</td>
<td>15.8</td>
<td>1.3</td>
<td>100.092</td>
<td>7800</td>
</tr>
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The exhaustion time, which marks the end of the loading cycle under each option, was taken as that time when the concentration in the feed tank was practically constant for batch operation and the time when effluent concentration reached 93-96% of the influent concentration with continuous contact which may be determined from the breakthrough profiles. The liquid phase concentrations in time in the batch mode and the breakthrough profiles for continuous operation are given in Figure 2 to show that two days was necessary for batch loading as operation time while a maximum of 10 hours was enough for continuous loading.

The surface capacities calculated from Figure 2. are presented in Figure 3. and Table 3. Surface capacities were 30.1-38.5 mg NH₄/g clinoptilolite and 0.44-0.66 mg PO₄-P/g clinoptilolite for the continuous system, while it was 9.3-25.0 mg NH₄/g clinoptilolite and 0.33-1.30 mg PO₄-P/g clinoptilolite for the batch mode. As can be observed, the highest surface capacity was 38.5 mg NH₄/g clinoptilolite with 90 minutes contact time for the continuous mode. On the other hand, the highest surface capacity for the batch operation was 25.0 mg NH₄/g clinoptilolite with 40 mg NH₄/g clinoptilolite initial ammonium loading. This showing that under all circumstances surface capacity was lower in the batch mode as compared to the continuous one, as in the continuous mode all were higher than 30 mg NH₄/g clinoptilolite. The results indicated that surface capacities were remarkably higher for nitrogen when continuous mode was employed, while for phosphorous batch operation gave slightly better outcomes. The reason for the difference between surface capacities for batch and continuous modes is that clinoptilolite is in contact with the same high influent concentration in the continuous mode while the liquid
phase concentrations keep decreasing in time in the batch mode. Therefore surface concentrations with highest liquid phase concentration as in the case of continuous operation will be expected to be higher.

It was previously stated that two days was necessary for batch loading while maximum 10 hours was enough for continuous loading as operation time. The lowest surface capacity, 9.3 mg NH₄/g clinoptilolite, was observed with 10 mg NH₄/g clinoptilolite initial loading in the batch mode, and this capacity could be attained in an operation time of 24 minutes with 30 minutes contact time in the continuous mode. While a maximum of 25 mg NH₄/g clinoptilolite surface capacity with 40 mg NH₄/g clinoptilolite initial loading in the batch mode could be achieved in 3 days, 2 hours was enough to attain the same value in the continuous mode with 30 minutes contact time. The results show that operation times were remarkably lower for the continuous mode, which will provide advantages in terms of sizes and operational costs.

![Figure 2. Liquid phase concentration in time for batch operation (a), the breakthrough profile for continuous operation (b)](image)

From the stand point of surface capacities and operation times, it is clear that continuous mode seems preferable over batch operation for nutrient recovery from human urine with clinoptilolite through ion exchange/adsorption. However when residuals, in this case residual liquid phase, i.e. human urine, are considered, continuous operation may be disadvantageous. This may be an important issue when pollution control is considered rather than or in addition to nutrient recovery.

Previous work on the impact of initial ammonium loading had shown that although surface concentrations increase with increased initial loadings, removal efficiencies from the liquid phase are lower and residual liquid phase concentrations are higher for higher initial loadings for batch systems (Beler Baykal et al., 2009). This present work provides support for these
findings. Ammonium removal efficiencies were 60-93% for the batch mode and 48-60% for the continuous one. The lowest ammonium removal efficiency for the batch mode was achieved as the highest value in the continuous mode and phosphorous removal efficiencies in the batch mode were at least 3 times higher than those in the continuous mode.

Figure 3. Surface ammonium concentrations/surface capacities in batch operation (a) and surface capacity in continuous operation (b).

Table 3. Surface ammonium concentration of clinoptilolite for batch and continuous operation

<table>
<thead>
<tr>
<th>Initial NH$_4$ loading (mg/g clinoptilolite)</th>
<th>Batch Surface capacity (mg NH$_4$/g clinoptilolite)</th>
<th>Contact time (min)</th>
<th>Continuous Surface capacity (mg NH$_4$/g clinoptilolite)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg NH$_4$/g clinoptilolite</td>
<td>mg NH$_4$/g clinoptilolite</td>
<td>mg PO$_4$-P/g clinoptilolite</td>
<td>mg NH$_4$/g clinoptilolite</td>
</tr>
<tr>
<td>--------------------------------------------</td>
<td>-------------------------------------------</td>
<td>------------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>10</td>
<td>9.3</td>
<td>0.33</td>
<td>30</td>
</tr>
<tr>
<td>15</td>
<td>12.8</td>
<td>0.39</td>
<td>65</td>
</tr>
<tr>
<td>20</td>
<td>16.6</td>
<td>0.63</td>
<td>90</td>
</tr>
<tr>
<td>25</td>
<td>17.4</td>
<td>0.71</td>
<td>120</td>
</tr>
<tr>
<td>30</td>
<td>18.0</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>25.0</td>
<td>1.33</td>
<td></td>
</tr>
</tbody>
</table>

Additionally, the results of this work presented in Table 4, have shown that residual liquid phase concentrations were 3086-4188 mg NH$_4$/g and 170-194 mg PO$_4$-P/L on a collective basis for the continuous mode, and 524-3020 mg NH$_4$/L and 2-57 mg PO$_4$-P/L for the batch mode, indicating that residual nutrient concentrations are higher in the continuous mode.

In summary, despite lower removal efficiencies and higher residual liquid phase concentrations, continuous mode is more preferable than batch mode in terms of surface capacities of nitrogen and operation times. The benefits of continuous operation in terms of sizes and costs in an actual application are addressed elsewhere (Allar Emek and Beler Baykal, 2016). As the main target
of this work was to attain higher surface capacities to recover higher quantities of plant nutrients as fertilizer, the continuous system provided a distinct advantage.

**Table 4.** Summary of liquid phase NH₄ and PO₄ concentrations and removal efficiencies (I-initial, R-residual concentrations)

<table>
<thead>
<tr>
<th></th>
<th>Batch system</th>
<th>Continuous system</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial loadings, mg NH₄/g clinoptilolite</td>
<td>Contact times, min</td>
</tr>
<tr>
<td></td>
<td>10 15 20 25 30 40</td>
<td>30 65 90 120</td>
</tr>
<tr>
<td>CI, mg NH₄/L</td>
<td>7175 6900 8000 7175 7100 8100</td>
<td>7800 7750 8125 7800</td>
</tr>
<tr>
<td>Cr, mg NH₄/L</td>
<td>524 1010 1330 2196 2832 3020</td>
<td>3086 3907 4188 3852</td>
</tr>
<tr>
<td>Removal, %</td>
<td>93 85 83 69 60 63</td>
<td>60 50 48 51</td>
</tr>
<tr>
<td>CI, mg PO₄-P/L</td>
<td>261 220 263 261 257 274</td>
<td>234 246 227 234</td>
</tr>
<tr>
<td>Cr, mg PO₄-P/L</td>
<td>26 42 12 57 44 2</td>
<td>194 176 170 174</td>
</tr>
<tr>
<td>Removal, %</td>
<td>90 81 95 78 83 99</td>
<td>17 28 25 26</td>
</tr>
</tbody>
</table>

**Conclusion**

In conclusion, continuous systems approach exhaustion in a much shorter time for nitrogen and phosphorous recovery from source separated human urine. Under no circumstances were operation times higher than 10 hours in the continuous mode as opposed to 2 days in the batch operation. Moreover, surface capacities of ammonium reflecting the amount which could be recovered per gram of clinoptilolite were higher when the mode of contact was continuous. This is expected to reflect into smaller sized columns and thus lower costs as advantages of the continuous operation. However, removal efficiencies were higher and the cumulative concentrations in the remaining liquid phase were lower in batch operation indicating that it is more advantageous for those aspects. All in all, continuous contact seems more plausible when the primary aim of processing is nutrient recovery for further use as fertilizer, especially when production of nitrogen fertilizers is intended.

**References**


Simultaneous municipal waste-activated sludge stabilization and direct power generation by a novel reactor named AMFD

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Keywords: reuse, energy recovery, waste management, waste-activated sludge, aerobic stabilization, direct power generation

Abstract

In this study, in order to approach an innovative method of energy recovery as well as waste management, a novel reactor has been designed, built and investigated in the laboratory. The main goal of our investigations was to reach effective stabilization of municipal waste-activated sludge and harvesting direct electrical energy by the reactor, in the same time. According to the results, the optimized intervals of operational parameters for electricity generation comply with the volatile and total suspended solids (VSS and TSS) removal efficiency. AMFD reactor showed its best behavior in temperature range from 35 to 45 °C and the catholyte and anolyte pH near to 7. In temperatures lower than 5 °C and higher than 65 °C, and strong acidic or basic conditions, the progress of both stabilization and electricity generation processes are negligible. The reactor is able to remove about 55% and 40% of VSS and TSS, respectively, and also, produce about 4.5 W electrical power per cubic meter of the anolyte in its best operational conditions.

1. Introduction

It is completely accepted that interest in environmental issues is continously increasing currently. At the same time, environmental issues have gradually been developed with concepts, such as sustainable development, which implies not only ecological, but also economic and social responsibilities (Fytili and Zabaniotou, 2008). The United States Environmental Protection Agency (US EPA) has developed incorporation of familiar concepts of efficiency like a water-wise energy sector as well as an energy-wise water sector, consideration of wastewater and waste sludge as a resource, and unified resource planning and recognition of the societal benefits, as principles for an integrated energy-water Future (US EPA guidelines, 2012). In this regard, reuse is one of the most important strategies that has been considered by urban water, wastewater and/or stormwater managers in order to improve the existing systems energy efficiency (Murphy and mc Keogh, 2006; Kelly and He, 2014; Monzo et al., 2003). According to remarkable characteristics of municipal wastewater sludge, attentions have been concentrated on the reuse of this material (Liu, 2003; Perez-Elvira et al., 2006; Appels et al., 2008; Murphy and mc Keogh, 2006; Logan, 2008) and various technologies that offer recovering energy from sludge, have been eventuated from these studies (Logan et al., 2005, Chaudhuri and Lovely, 2003; He et al., 2008, Dentel et al., 2004; Lee et al., 2011). The United States produced 7.6 million tons of dry sludge in 2005 (Cusido et al., 2003). In the same year, the EU produced 10 million tons of dry sludge in 2005 (Wang et al., 2008) and China produced 1 million tons of dry sludge (Burke et al., 2003). In addition, the quantity of generated sludge has increased annually as a result of the development of sewage treatment systems and speeded
up noticeably in recent years. The nature of the present wastewater treatment systems is such that toxic pollutants are concentrated in the sludge, together with a large fraction of pathogens. Therefore, such huge amounts of munisipale sludge cannot be disposed without appropriate treatments (Da Ros et al., 2016; Badalians Gholikandi, 2015). Parallel to the improvement of the effluent quality, a growing awareness of the problems associated with the municipal waste sludge came into the front. Continuous increase in sludge production, the high costs of sludge treatment and stabilization, and the risks that sewage sludge is capable to have on the environment and human health, are some of these problems.

On the other hand, municipal waste sludge contains high levels of organic matters and is regarded as an available renewable resource. Lots of studies have been carried out in order to reuse or reclaim the municipal waste sludge, such as biogas production, anaerobic fermentation for hydrogen production, aerobic compost for fertilizer production, and so on. But, the limitations of common energy recovery methods and their noticeably low conversion efficiencies to electricity (as one the most desired forms of energy), made researchers to think for new technologies to generate electricity directly from waste materials such as waste-activated sludge (Jiang et al., 2009; Goud and Mohan, 2011; Chadhury and Lovely 2003). Direct electricity generation from biomass (which municipal waste sludge is belonged to) is performed by converting chemical energy of organic matters to electricity via electrogenic microorganism through bioelectrochemical reactions. These systems are capable of simultaneously treating organic wastes and generating electricity (Aelterman et al., 2006; Tao et al., 2015; Logan et al., 2006; Zhang and Angelidaki, 2013). In this study, in order to approach an innovative method of energy recovery, a novel reactor has been designed, built and investigated in the laboratory. This reactor is able to receive waste-activated sludge as feed and generate direct electrical power simultaneous with sludge aerobic digestion. According to potential advantages of aerobic stabilization of the sludge (He et al., 2008), we chose this process as the main digestion process and integrated it to a two chamber microbial fuel cell, to make the novel reactor, named aerobic microbial fuel digester (AMFD). In order to decrease the number of required experiments and include the influences of individual factors as well as their interactive influences Response Surface Methodology (RSM) has been proposed. RSM helps researchers to design experiment, build models, evaluate the effects of several factors, and attain the optimum conditions for desirable responses in addition to reducing the number of experiments (Ghaffari et al., 2014). Experimental designing and optimization process carried out by Design Expert software and the effect of operational parameters on sludge digestion efficiency and amount of generated power have been investigated. VSS and TSS removal efficiencies have been considered as the reactors aerobic stabilization process and power density has been considered as its electricity production.

2. Material Methods

Sewage sludge was collected from the secondary sedimentation tank of Mahallati Municipal Wastewater Treatment Plant which is located in north east of Tehran and treats 4,800 m$^3$ wastewater per day. Table 1 demonstrates the characterization of investigated sludge. The reactor contains two chambers as anode and cathode which are separated by a proton exchange membrane (PEM) (PEM, Nafton TM 117, Dupont Co., USA). Each chamber contained two electrodes and the distance between the electrodes was 80 mm. The surface area of the electrodes were about to 400 mm$^2$. Each chamber had a volume of 2500 mL. Cathode chamber
aerated very well by two aerators. The content of anode chamber was blended by a magnetic bar mixer. The volume of the chambers liqied kept unchanged by adding deionized water was supplied at times in order to keep the volume of the mixed liquid. All of the chemicals like caustic soda (NaOH) and concentrated sulfuric acid (H₂SO₄) have been provided from Merck® Co. Due to the effect of the dissolved oxygen (DO) on both processes of the reactor, the concentrations of DO in cathode and anode chambers were controlled.

Table 1: the characterization of investigated municipal waste sludge in this study

<table>
<thead>
<tr>
<th>Item</th>
<th>Property</th>
<th>unit</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pH</td>
<td>-</td>
<td>6.5-7.5</td>
</tr>
<tr>
<td>2</td>
<td>Temperature</td>
<td>°C</td>
<td>18-25</td>
</tr>
<tr>
<td>3</td>
<td>Chemical Oxygen Demand (COD)</td>
<td>mg/L</td>
<td>6000-11200</td>
</tr>
<tr>
<td>4</td>
<td>Volatile Suspended Solids (VSS)</td>
<td>mg/L</td>
<td>3500-7800</td>
</tr>
<tr>
<td>5</td>
<td>Total Suspended Solids (TSS)</td>
<td>mg/L</td>
<td>4100-8550</td>
</tr>
</tbody>
</table>

Experiments were carried out in triplicate and all results are the means of replicate analyses. A multi-meter has been used (2700, Keithley, OH, USA) with a voltage across resistor, as well as a data acquisition system which was connected to a computer. All tests are conducted according to standard methods (American Public Health Association (APHA) 1999). The experiments have been designed by Design Expert software according to the valid ranges of the operational parameters and 13 experiments have been carried out in order to investigate the effects of operational parameters on responses.

3. Results and Discussion

3.1 RSM optimization results

Figure 1 and Figure 2 show the results of RSM optimization process for the VSS and the generated electrical power density of AMFD reactor. According to the figures, this reactor demonstrated its best performance in temperature range from 35 to 45 °C and the catholyte and anolyte pH near to 7. Also, in the temperatures lower than 5 °C and higher than 65 °C, and strong acidic or basic conditions, the progress of both stabilization and electricity generation processes are negligible. According to the results, the reactor is able to produce about 4.5 W electrical power per each m³ of the anolyte in its best operational conditions.

Figure 1. The VSS removal efficiency of AMFD reactor versus temperature and pH (obtained from RSM)

Figure 5. The generated electrical power density of AMFD reactor versus temperature and pH (obtained from RSM)
3.2 Evaluation the validity of the models
In order to check the compatibility of the results which have been provided from RSM models and actual results, extra experiments (other than the experiments of design expert) have been carried out in the laboratory and their obtained data have been compared with the model’s output. Figure 3 and Figure 4 show the results of experiments in various temperatures (and approximately constant pH value) and different pH values (and constant temperature) in the laboratory, respectively. According to Figure 3, the reactor’s best VSS and TSS removal efficiency was about $42\pm2\%$ and $35\pm2\%$, respectively at $45\, ^\circ C$.

![Figure 3](image1.png)  ![Figure 4](image2.png)

**Figure 3.** The removal efficiencies of AMFD reactor versus temperature  **Figure 4.** The removal efficiencies of AMFD reactor versus pH

Figure 4 represents that AMFD reactor reaches its best performance when the pH is about to 7 (the VSS and TSS removal efficiencies are about $45\pm2\%$ and $36\pm2\%$, respectively). The experimental results of the reactor’s generated power densities in various temperatures and approximately constant pH have been demonstrated in Figure 5. Also, Figure 6 shows the results of in different pH values and constant temperature.

![Figure 5](image3.png)  ![Figure 6](image4.png)

**Figure 5.** The generated power densities and current densities curves of AMFD reactor in various temperatures  **Figure 6.** The generated power densities and current densities curves of AMFD reactor in various pH values
The investigations of temperature effect on the reactor’s performance showed that the highest generated electrical power density of the reactor have been observed at 35 °C which was about 4.3 W/m². At 15 °C the current density produced by the reactor ranged from 0.262 to 21.55 mA/m² and the power density varied 68.233 to 3233.994 mW/m³. By increasing the temperature from 15 to 25 °C, the values of produced current density and the generated power density have been risen. Increasing temperature from 25 to 35 °C, noticeably promotes the produced current density, and the generated power density to their maximum observed values of this study. At 35°C, the current density ranged from 0.061 to 25.14 mA/m² and the power density changed from 26.40 to 4248.1 mW/m³. When the temperature increases from 35 to 45 °C, the values of produced current density and generated power density decreases compared with 35 °C, but they are still higher than 25 °C. In other words, the upward trend of produced electricity via temperature reverses in higher temperature than 35 °C.

Also, the studies on pH effect on the reactors electricity generation performance showed that the generated power density in neutral pH conditions is remarkably higher than other conditions, shown in Figure 6. As mentioned before, during the experiments, the temperature was held 35 °C which AMFD reactor demonstrated the best performance of electricity generation. According to Figure 6, in pH values lower than 3, considerable amounts of current density did not observe as well as generated power density. By increasing pH value to 3, the process started to progress and generate electricity. When the value of pH increased to 5, the electricity generated by the process showed considerable growth. Consistent with the observations, electricity generation by reactor enhanced by increasing the value of pH from 5 to 7 as well as from 3 to 5. By increasing the pH value from 7 to 9, the amounts of produced current density and the generated power density have been decreased. In other words, the upward trend of these parameters via the pH value of the catholyte reversed to downward by increasing it from 7 to 9.

**Conclusion**

A novel reactor has been designed, built and investigated in order to reach an innovative method of energy recovery as well as waste management, in the laboratory. The main goal of our investigations was to approach effective stabilization of municipal waste-activated sludge and harvesting direct electrical energy by the reactor, in the same time. Regarding the obtained results from the optimization models and experiments, the optimized intervals of operational parameters for electricity generation comply with the suspended solids (VSS and TSS) removal efficiency. Also, Comparison the experimental results with the outputs obtained from optimization, proved this fact that the designed models are reliable enough to be considered in prediction or investigation the performance of AMFD reactor in different operational conditions.

**References**


Heavy metals removal from waste-activated sludge employing Fered-Fenton electrochemical advanced oxidation technology with the aim of agricultural land application

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*aWater and Environmental Engineering Faculty, Shahid Beheshti University A. C., Tehran, Iran (g.badalians@yahoo.com).

Keywords: Waste-activated sludge treatment; heavy metals removal; electrochemical advanced oxidation process; Fered-Fenton technology; land application

Abstract

In the past few years, in order to reduce and mitigate expected sludge health risks due to land application, a number of methods for elimination of heavy metals within wastewater sludge have been examined. Due to the various disadvantages of conventional sludge stabilization processes, it is becoming increasingly apparent that novel efficient technologies are essential for preventing serious problems during eco-biological cycle. The Fered-Fenton technology can be applied in an efficient manner to stabilize waste-activated sludge thus leading to a final product that which can be reused as an organic soil fertilizer. In this research, the final product resulted from a lab-scale Fered-Fenton reactor was investigated so as to evaluate the quality of the treated waste-activated sludge for agricultural land application. SO, the efficiency of this process for the removal of chromium, molybdenum, copper, lead, zinc, and mercury (frequent heavy metals) at three different operating pH values equal to 3, 5 and 7, and supplying current densities equal to 450, 650 and 850 mA, have been evaluated. According to the results the best approach for the removal of heavy metals occurred at pH value equals to 3 and also heavy metals concentrations in the stabilized municipal waste-activated sludge met current legal limits for agricultural land application. The test results indicate the removal of chromium, molybdenum, copper, zinc, lead and mercury to the amount of 90%, 48%, 91%, 70%, 80% and 62%, respectively. Therefore, the treated waste-activated sludge by the Fered-Fenton process is able to be used to agricultural soils.

1. Introduction

Conventional activated sludge wastewater treatment method lead to the generation of a large amount of waste-activated sludge (WAS), which contains a noticeable concentrations of heavy metals, and poorly biodegradable organic compounds. Since some alternatives of WAS final disposal may cause potential threats to human health and environment (Méndez et al., 2012; Zielińska and Oleszczuk, 2015), it is necessary to investigate promising novel approaches with the aim of its efficient stabilization (Braguglia et al., 2012; Yu et al., 2010). According to the fertilizing properties of municipal waste-activated sludge, its agricultural land application is an interesting environmental and economical alternative (Passuello et al., 2012; Beauchesne et al., 2007; Escala et al., 2013; Gorguener et al., 2015). Definitely, there is great concerning about land application of sludge, due to the potential existing pollutants (Clarke et al., 2010; De la Torre et al., 2011) and the related possible soil, ground water and crops contamination (Passuello et al., 2010; Carrère et al., 2010). Due to the various disadvantages of conventional
sludge stabilization processes (Metcalf and Eddy, 2003; Turovskiy and Mathai, 2006; Kelessidis and Stasinakis; 2012), it is becoming increasingly apparent that novel efficient technologies are essential for preventing serious problems during eco-biological cycle (Alvarez et al., 2002). Thus, sludge treatment systems must provide a final product suitable for agricultural land application and fulfilling legislation requirements (Jones-Lepp and Stevens, 2007). In recent years, several methods have been employed to sludge pre-treatment and stabilization based on electrochemical advanced oxidation processes (EAOPs) (Song et al., 2010; Bureau et al., 2012; Badalians et al., 2014; Mo et al, 2015). The main reactions (Eqs. 1 and 2) involved in this method are as follows:

\[
\text{Fe}^{2+} + H_2O_2 \rightarrow \text{Fe}^{3+} + OH^- + OH^0
\] (1)

\[
\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}
\] (2)

Furthermore, Gholikandi et al. (2014) in a previous study focused on the removal of sludge volatile suspended solids (VSS) as an indicator of the WAS organic matters content. This study was conducted to evaluate the Fered-Fenton process efficiency in removal of frequent heavy metals (chromium, molybdenum, copper, lead, zinc, and mercury) at three different operating pH values equal to 3, 5 and 7, and supplying current densities equal to 450, 650 and 850 mA and fecal coliforms inactivation as well the process capability to preserve the sludge fertilizing properties (i.e. nitrogen, phosphorus, natrium, potassium, and calcium) with the aim of agricultural land application.

2. Material Methods

The investigations were conducted in a laboratory scale setup (Fig. 1). The reactor cell was made of plexiglass with a volume equals to 0.9 L. Graphite electrodes (i.e. two anodes and two cathodes) were employed because of its chemical inert and decomposable property. The electrodes dimension was 1 mm× 140 mm× 60 mm, placed at a distance of 1.5 cm from one another (Nidheesh and Gandhimathi, 2012). The depth of the electrodes placed in the sludge was 100 mm and the contact surface was 100 mm× 60 mm. An electrical mixer (Zheng, zs-ri, 6(V), DC, 3.66 rpm) was utilized accordingly. A digital laboratory model power supply (Mps, DC-3003D, 0-30 (A), 0-30 (V)) has been used for the amperage adjustment.

![Figure 1. Fered-Fenton reactor in lab-scale and the related reactions](image-url)
The chemicals used in this work included ferrous sulfate and hydrogen peroxide as Fenton reagent, and concentrated sulfuric acid and sodium hydroxide (soda) for pH adjustment. Thus, CuSO₄, Pb(NO₃)₂, HgSO₄, K₂Cr₂O₇, Cl₂Zn and (NH₄)₆Mo₇O₂₄ were added to WAS samples for making alterations to initial heavy metals ion concentrations. The chemicals from Merck® Co. were used and the treated samples were filtered by using Whatman® filter papers (No. 42). Table 1 shows the specifications of the characterized municipal raw waste-activated sludge samples used in this study. The samples pH values were adjusted by adding an adequate dosage of sulfuric acid and soda. Then, samples containing the investigated heavy metals with the initial synthetically added concentration were placed in the Fered-Fenton lab-scale reactor cell. Then, ferrous sulfate, hydrogen peroxide, and Fenton's reagents (FeSO₄ and hydrogen peroxide (H₂O₂) were added to the reactor cell. Thereafter graphite plate electrodes were connected to the laboratory model DC power supply system and voltage and current were adjusted. Stabilized WAS samples were analyzed by analytical methods referred to the standard methods for the examination of water and wastewater (APHA, 1999). The concentrations of the heavy metals were determined by means of Inductively Coupled Plasma (ICP) Model Varian 710. Concentrations of the other investigated ions were measured by utilizing an Ion Chromatography Model Metrohm-IC850. The most probable number (MPN) method was used for microbial investigations (APHA, 1999). All experiments were repeated three times.

Table 1. The characteristics of the municipal waste-activated sludge samples

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.53-7.31</td>
</tr>
<tr>
<td>Temperature(°C)</td>
<td>13.5-15.7</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>5768-10985</td>
</tr>
<tr>
<td>SCOD (mg/L)</td>
<td>38-67</td>
</tr>
<tr>
<td>VSS (mg/L)</td>
<td>3136-6682</td>
</tr>
<tr>
<td>VS (mg/L)</td>
<td>3201-6810</td>
</tr>
<tr>
<td>TS (mg/L)</td>
<td>4375-8825</td>
</tr>
<tr>
<td>TSS (mg/L)</td>
<td>4085-8537</td>
</tr>
<tr>
<td>VSS/TSS</td>
<td>0.76-0.78</td>
</tr>
</tbody>
</table>

3. Results and Discussion

The main hazard associated with waste-activated sludge application on agricultural land is the potential long term accumulation of toxic materials (Xu and Li, 2013). The results of the investigated heavy metals removal from municipal waste-activated sludge employing Fered-Fenton method are presented in Figures 2, 3, 4, 5, 6, and 7. The initial concentration of each heavy metal was considered at maximum level corresponding to the American environmental protection agency standards (USEPA, 1995).

3.1. Chromium

Depending on the pH of the medium, intensity of applied current density, and the electrode material used, electrochemical reduction of hexavalent chromium may occur in several ways. Because of the initial concentration resulted from adding K₂Cr₂O₇ to the sludge sample, total chromium existed as hexavalent chromium. Fe²⁺ cations added as Fenton reagent was the another contributor to hexavalent chromium reduction. In addition, the reduced Cr³⁺ could be electrodeposited on the cathode or be held in the cathodic layer (Barrera-Díaz et al., 2012; Yin et al., 2014). However, further reactions known as side reactions (i.e. hydrogen evolution) can occur in the proximity of the cathode resulting in loss of cathodic current efficiency. The most driving parameter in chromium electro-reduction is the pH value of the medium. The results plotted in Figure 2 show that the maximum chromium removal (i.e. 90 %) is achieved under acidic condition (i.e. pH value equals to 3). At higher pH values, chromium species occur in
chromic (Cr$^{3+}$) form and the reaction between Cr$^{3+}$ and OH- causes chromium hydroxide (Cr(OH)$_3$) generation. Under neutral conditions, the hydrated Cr$^{3+}$ ion precipitates as Cr(OH)$_3$ to the sludge cake. It is noticeable that increasing current density results directly in decreasing the concentration of hexavalent chromium ions on the electrode surface (Barrera-Díaz et al., 2012).

### 3.2 Molybdenum

Due to the existing high concentration of Fe$^{2+}$ ions as Fenton reagent, Mo$^{7+}$O$_{24-6}$ species become converted into the predominant MoO$_{4-2}$ species at a pH value equals to 5 to 7. Transformation of MoO$_{4-2}$ to molybdenum as a result of electrochemical reduction at the electrode surface and finally, molybdenum electro-deposition on the cathode surface leads to removal of the molybdenum from the sludge (Syed et al., 2015; Saji et al., 2012). Figure 3 shows that the maximum molybdenum removal (i.e. 48 %) occurs at pH value equals to 5 and current density equals to 450 mA.

![Figure 2](image2.png)

**Figure 2.** The effect of pH value and current density on the chromium removal process efficiency, [Fe$^{2+}$]/[H$_2$O$_2$]=0.58, retention time= 6(h), [H$_2$O$_2$]=1568(mg/L), initial chromium concentration = 1000±80(mg/kg)

![Figure 3](image3.png)

**Figure 3.** The effect of pH value and current density on the molybdenum removal process efficiency,[Fe$^{2+}$]/[H$_2$O$_2$]=0.58, retention time= 6(h), [H$_2$O$_2$]=1568(mg/L), initial molybdenum concentration = 75±20 (mg/kg)

### 3.3 Copper

During electrochemical deposition of the copper ion, two main reduction reactions occur, i.e. formation of metallic copper and cuprous oxide Cu$_2$O (Lambert et al., 2014). It was observed that at the pH value equals to 3, the rate of Cu$^{2+}$ reduction is more than the higher pH values (Fig. 4). The removal efficiency increased with increment of current density from 450 to 850 mA. The significant efficiency of this approach in copper ions removal can be explained on the basis of the high potential of Cu$^{2+}$ reduction (Fu and Wang, 2011). The maximum copper removal (i.e. 91%) occurs at the pH value equals to 3 and current density equals to 850 mA.

### 3.4 Zinc

As Figure 5 reveals, the process efficiency declined with increment of pH value from 3 to 7. The increment of current density from 450 to 850 mA causes increasing efficiency. By applying adequate current density to the system, the Zn$^{2+}$ and H$^+$ ions reduction occurs in the cathode proximity and leads to the metallic zinc ions removal from the sludge. Therefore, electro-deposition of the zinc on the cathode surface and the simultaneous evolution of H$^2$ gas were observed (Kavitha et al., 2014). The maximum zinc removal (i.e. 70%) occurs at pH value equals to 3 and current density equals to 850 mA.

### 3.5 Lead

Due to the Fenton process occurrence, the formed OHads particles chemisorbed on the electrode surface. In the next stage, these particles interact with lead ions forming a soluble intermediate product Pb(OH)$_{22-}$, which is oxidized electrochemically by transfer of the second electron, generating a soluble oxygenated Pb(OH)$_{22+}$ compound. Finally, the resulted PbO$_2$, as the
product of hydrogen ions dissociation, settled on the electrodes surface, i.e. lead dioxide electrodeposited on cathode surface, which depends on the supplied current density (Velichenko and Devilliers, 2007). The maximum lead removal efficiency (i.e. 80%) was observed at pH value equals to 3 and current density equals to 850 mA (Fig. 6). While the pH value increased from 3 to 7, the removal process occurrence declined considerable.

3. 6. Mercury
The operating pH value influences the mercury ions removal process significantly (Salinas et al., 1999). If the pH value of the medium increases from 3 to 7, the removal efficiency decreases (Fig. 7). Maximum efficiency of the system (i.e. equals to 62%) was achieved at the pH value equals to 3 and applied current density equals to 850 mA. This is caused by increasing pH value (up to pH of 7) that leads to the stabilization of mercury in the form of Hg(SO₃)₂⁻ in the presence of sulfate anions, Hg(OH)⁺ and Hg(OH)₂ (Ochoa-González et al., 2013). Optimum operating conditions for heavy metals removal, optimum effluent concentrations of the Fered-Fenton lab-scale reactor and ceiling concentration limits regarding agricultural land application are listed in Table 2.

Conclusions
In this research, for the first time, the process efficiency of the Fered-Fenton electrochemical advanced oxidation method has been studied in heavy metals removal with the aim of the treated waste-activated sludge agricultural land application, as a promising technical and environmentally friendly method of enhancing waste-activated sludge stabilization occurrence. The results have proved the high efficiency of this method in considerably reducing the heavy metals content (chromium, molybdenum, copper, lead, zinc, and mercury) with the US EPA regulations. It must be noticed that the treated sludge is in most cases acidic and consequently, must be neutralized, i.e. addition of lime or dolomite at pH value equals to 3 and 5 before the application. The next step would be to carry out more studies in order to optimize the energy consumption rate.
Table 2. Optimum operating conditions for heavy metals removal from waste-activated sludge employing Fered-Fenton method

<table>
<thead>
<tr>
<th>Metal</th>
<th>Optimum condition</th>
<th>Initial concentration (mg/kg)¹</th>
<th>Effluent concentration (mg/kg)</th>
<th>Maximum Concentration Limits (mg/kg)²</th>
<th>Clarification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>pH = 3, current density = 850(mA)</td>
<td>1000±80</td>
<td>100±10</td>
<td>3000</td>
<td>Lower limit</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>pH = 5, current density = 450(mA)</td>
<td>75±20</td>
<td>39±5</td>
<td>75</td>
<td>Lower limit</td>
</tr>
<tr>
<td>Copper</td>
<td>pH = 3, current density = 850(mA)</td>
<td>7600±100</td>
<td>684±50</td>
<td>4300</td>
<td>Lower limit</td>
</tr>
<tr>
<td>Zinc</td>
<td>pH = 3, current density = 850(mA)</td>
<td>13000±200</td>
<td>3900±200</td>
<td>7500</td>
<td>Lower limit</td>
</tr>
<tr>
<td>Lead</td>
<td>pH = 3, current density = 850(mA)</td>
<td>3400±50</td>
<td>680±50</td>
<td>840</td>
<td>Lower limit</td>
</tr>
<tr>
<td>Mercury</td>
<td>pH = 3, current density = 850(mA)</td>
<td>500±40</td>
<td>190±20</td>
<td>57</td>
<td>Larger limit</td>
</tr>
</tbody>
</table>

¹,² referred to USEPA (1995)

References


Zielińska, A., & Oleszczuk, P., 2015, The conversion of sewage sludge into biochar reduces polycyclic aromatic hydrocarbon content and ecotoxicity but increases trace metal content. Biomass and Bioenergy, 75, 235-244.
Fered-Fenton Electrochemical Advanced Oxidation Process for Waste-activated Sludge Stabilization and Reuse: Macronutrients Preservation and Microbial Inactivation

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Keywords: Waste-activated sludge treatment; Fered-Fenton method; agricultural land application; nutrients preservation; fecal coliforms inactivation.

Abstract

In this study, we focused on the removal of sludge volatile suspended solids (VSS) as an indicator of the WAS organic matters content. The aforementioned research reported that VSS removal efficiency of 78, 60, and 55% can be reached at different pH values equal to 3, 5, and 7 under operational conditions as follows: [Fe]/[H₂O₂]=0.60, [H₂O₂]=1250 (mg/L), retention time= 240 (min), and current density= 600-800 (mA). Moreover, reusing the stabilized sludge with this system for agricultural uses, under the optimized situation, was examined. In addition, the C/N ratio of treated sludge from 13.7 at pH of 7 decreased to 12.2 at pH of 5 and 8.47 at pH of 3. The investigated method significantly eliminated fecal coliforms (i.e. more than 99.9%). Therefore, at pH values equal to 3, 5, and 7, the fecal coliforms concentration meets the Class A requirements regulated in the US EPA standard, so results of Fered-Fenton showed that this system not only has a good ability for stabilizing the sludge, but also the output sludge could be used as a fertilizer in agricultural uses.

1. Introduction

Treatment and safe disposal of hazardous materials (waste, excess sludge, leachate, etc.) is an imperative and inevitable measure to preserve the environment. Nowadays, wastewater treatment systems are used widely by activated sludge method, which results in producing a large amount of biological excess sludge that is a threat to human health (Tokomuro et al., 2009). With the increasing growth of biological excess sludge has made it one of the most important and most critical environmental issues (Xu et al., 2012). Management, consolidation, and disposal of sludge are considered as key and strategic goals in wastewater treatment systems (Yu et al., 2010). The sludge contains hazardous substances, such as chemical organic materials, heavy metals, and pathogens that if are not stabilized and disposed safely, they will enter the food chain and endanger the human health (Wang et al., 2013). The overall objective of stabilizing the sludge includes removal of organic matter, sludge volume, heavy metals and pathogens and converting them into useful sources (Weng et al., 2014).

Recently, the use of the advanced oxidation processes (especially Fenton) has been taken into consideration in wastewater treatment (Gu et al., 2013). Performance efficiency of advanced oxidation processes in degradation of biological organic compounds, sewage sludge
contaminants, and soil has caused attractiveness of such methods (Shen et al., 2013). Advanced oxidation processes are those in which adequate hydroxyl radical is produced (Anotai et al., 2010). Hydroxyl radical which is one of the most impressive oxidizing agents in water and environment, reacts non-selectively \((E^0 = 2.87)\) (Tao et al., 2013). One of the most common advanced oxidation methods is Fenton process that has advantages such as low initial cost, easy operation and production of non-toxic byproducts (Anotai et al., 2010). In this study combined Fenton and electrochemical method was used in order to reduce sludge organic load (VSS: Volatile Suspended Solids). One of Fenton drawbacks is that the consumption rate of divalent iron ions (reaction 1) is faster than its reduction (reaction 2) (Babuponnusami and Muthukumar, 2012). To overcome this issue, the electrochemical method was used. This method increases the reduction rate of divalent iron by converting the trivalent iron ions to the divalent ones (reaction3).

\[
Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + O\cdot + H^+ \quad 53-76 M^{-1} \cdot S^{-1} \quad (1)
\]

\[
Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + ^0H_2O + H^+ \quad 0.01-0.02 M^{-1} \cdot S^{-1} \quad (2)
\]

\[
Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (3)
\]

In this study, the advanced Fered-Fenton oxidation process was used for sludge stabilization. The VSS removal was chosen as a criterion for stabilizing the sludge and the effect of important parameters in Fered-Fenton process (including pH, time, current density and the concentration of \(H_2O_2\) and \([Fe^{2+/H_2O_2}]\)) on VSS removal was studied. Moreover, the stabilized sludge with this system was examined for reuse and further the amount of nutrient conservation and pathogens removal in the stabilized sludge was determined.

2. Material Methods

The investigations were conducted in a laboratory scale setup. The reactor cell was made of Plexiglass with a volume equals to 0.9 L. Graphite electrodes (i.e. two anodes and two cathodes) were employed because of its chemical inert and decomposable property. The electrodes dimension was 1 mm× 140 mm× 60 mm, placed at a distance of 1.5 cm from one another (Nidheesh and Gandhimathi, 2012). The depth of the electrodes placed in the sludge was 100 mm and the contact surface was 100 mm× 60 mm. An electrical mixer (Zheng, zs-ri, 6(V), DC, 3.66 rpm) was utilized accordingly. A digital laboratory model power supply (Mps, DC-3003D, 0-30 (A), 0-30 (V)) has been used for the amperage adjustment. The chemicals used in this work included ferrous sulfate and hydrogen peroxide as Fenton reagent and concentrated sulfuric acid, and sodium hydroxide (soda) for pH adjustment. The chemicals from Merck® Co. were used and the treated samples were filtered by using Whatman® filter papers (no. 42). the specifications of the characterized municipal raw waste-activated sludge samples used in this study were determined and the results included: pH=6.53-7.31, Temperature\(^0\text{C}\)= 13.5-15.7, COD (mg/L)= 5768-10985, SCOD (mg/L)= 38-67, VSS ( mg/L)= 3136-6682, VS ( mg/L)= 3201-6810, TS (mg/L)= 4375-8825, TSS (mg/L)= 4085-8537 and VSS/TSS=0.76-0.78. The samples pH values were adjusted by adding an adequate dosage of sulfuric acid and soda. Then, ferrous sulfate, hydrogen peroxide, and Fenton's reagents (FeSO\(_4\) and hydrogen peroxide (H\(_2\)O\(_2\)) were added to the reactor cell. Thereafter graphite plate electrodes were connected to
the laboratory model DC power supply system and voltage and current were adjusted. Stabilized WAS samples were analyzed by analytical methods referred to the standard methods for the examination of water and wastewater (APHA, 1976). The most probable number (MPN) method was used for microbial investigations (APHA, 1976). All experiments were repeated three times.

3. Results and Discussion

3.1. Effecting factor on VSS removal

pH is one of the most important efficient parameters in Fenton process. The reactors laboratory investigations also demonstrate the maximum efficient VSS removal of up to 68% in the pH of range 3 (figure 1 diagram a). Furthermore, it was reported that the efficiency of the system will be reduced by decreasing the pH to less than 3, so that with pH =1 it will be reached to 54%. At the low values of pH, the iron species form stable complexes with H₂O₂, and as a result, the neutralization of iron catalysts occurs and the efficiency of the oxidation decreases considerably (Wang et al., 2010). The other reason is constancy of the hydrogen peroxide in the form of H₂O₂⁺ (Zhou et al., 2007), which results in the disinvolvedment of the H₂O₂ in the reaction 1 and the reduction of hydroxyl radical generation and thus causes the reduction of the VSS removal efficiency. By increasing pH from 3 to 5, the efficiency of the laboratory system reduces to 58% in pH=5. But in the pH of more than five, due to the unstable situation of hydrogen peroxide and transforming to water and oxygen, the efficiency of the system reduced even faster (Shemer and Linden, 2006). Increasing the electric current density results in the transformation of iron Fe³⁺ to iron Fe²⁺, thus Fenton process will be more effective and reaction 3 takes place (Zhang et al., 2007). As it is shown in figure 1 diagram b, when there is no current in the laboratory system, in practice only Fenton process exists and the efficiency of the system will be 22%. After making the electric current in the system the efficiency increases and in the current density of 600-800 mA the VSS removal efficiency reaches to 72% in the best situation. Increasing the current density up to 800 mA causes hydrogen reduction on the cathode electrode surface and prevents reduction of iron thus the VSS removal decreases as well. Figure 1 diagram c shows the impact of hydrogen peroxide on VSS removal. By increasing the concentration of hydrogen peroxide according to reaction 1, hydroxyl radical is produced and VSS removal is reduced. This process continues for the concentration of up to 1250 mg/lit which eventually reached a removal efficiency of 74%. Subsequently, the efficiency of the laboratory system decreased by increasing the hydrogen peroxide concentration. This process is due to consumption of hydroxyl radical by the extra hydrogen peroxide in the system which causes the reduction of VSS removal efficiency (Muruganandham and Swaminathan, 2004). The retention time because of energy consumption in the Fred-Fenton system is also of great importance and optimizing it will result in lower energy consumption. As figure 1 diagram d shows the maximum VSS removal efficiency will be reached within the first two hours of the test, which is approximately up to 50%. This is due to the high concentration of the biodegradable organic matters in the laboratory system. The efficiency of the laboratory system in the next two hours reached to 78%, and after that, no significant changes was observed.
The relationship between pH and VSS removal efficiency, constants: a hydrogen peroxide concentration of 1000 mg/L, a current density of 400 mA, ratio of [Fe^{2+}/H_{2}O_{2}]=0.45, a retention time of 180 minutes. (b). The relationship between current density and VSS removal efficiency, constants: a hydrogen peroxide concentration of 1000 mg/L, a pH value of 3, ratio of [Fe^{2+}/H_{2}O_{2}]=0.45, a retention time of 180 minutes. (c). The relationship between peroxide hydrogen concentration and VSS removal efficiency, constants: a pH value of 3, a current density of 600-800 mA, ratio of [Fe^{2+}/H_{2}O_{2}]=0.45, a retention time of 180 minutes. (d). The relationship between [Fe^{2+}/H_{2}O_{2}] ratio and COD removal efficiency, constants: a pH value of 3, a current density of 600-800 mA, a hydrogen peroxide concentration of 1250 mg/L, a retention time of 180 minutes. (f). The relationship between retention time and VSS removal efficiency, constants: a pH value of 3, a current density of 650 mA, ratio of [Fe^{2+}/H_{2}O_{2}]=0.60, a hydrogen peroxide concentration of 1200 mg/L.

3.2. Fertilizing property preservation
The process efficiency in sludge fertilizing property preservation was evaluated by investigating the total carbon (TC) and inorganic elements concentrations such as NO\textsubscript{3}\textsuperscript{−}, NH\textsubscript{4}\textsuperscript{+}, TN, TP, Na, K, and Ca. The total carbon concentration was considered as an indicator of existing organic material. Choosing pH value equal to 3 is because the maximum removal of VSS happens at this level of pH. The value of 5 for pH was a good choice because of the possibility of using it in the actual situation. Testing pH value equal to 7 was chosen because it does not need adding any extra chemical matter to arrange the pH.

Existing organic matter in soil improves the physical, chemical, and biological properties which are necessary to ensure soil fertility (U.S. EPA, 1995). The main agent of organics oxidation is the generated hydroxyl radical (OH\textsuperscript{\textbullet}) by the Fenton reaction (Eq. 1). It was investigated by several studies that the most efficient Fenton process can be occurred at a pH of 3 (Nidheesh and Gandhimathi, 2012). In this study, the maximum removal efficiency equals to 79.6% at the pH value of 3 was achieved. The removal efficiency decreased with increasing pH value (i.e.
45.7% at pH of 7). This can be justified with respect to a decline of the OH\(^0\) production during the occurrence of Fenton reaction (Fig. 2). In the present study, the nitrogen content of the raw and treated waste-activated sludge has been considered as nitrate (NO\(^3\)-) and ammonium (NH\(_4^+\)) ions. The maximum removals of the nitrate (i.e. 83.8%) and ammonium (i.e. 73%) were reached at pH equals to 3. An increase in pH value (up to 7) caused the reduction in nitrate and ammonium ions removal efficiency (i.e. 52.3% and 51.1%) (Figs. 2 and 3). The main cathodic reactions by the electrochemical reduction of nitrate ions to nitrogen gas and ammonia in acidic solution have been represented by Paidar et al. (Paidar et al., 1999), Kim et al. (Kim et al., 2006) and Mook et al. (Mook et al., 2012). The initial content of phosphorus in the raw sludge was 2.97±0.1 % of dry matter. The maximum removal (26 – 35%) was reached at pH of 3 by an addition of strong quantities of sulfuric acid for pH adjustment. This could be explained by P precipitation in the form of ferric phosphate. Thus, the generation of Fe\(^{3+}\) due to the Fenton reaction (Eq. 1) at high pH values resulted in enhancing the sludge phosphorus content (Fig. 2).

The initial content of the micronutrients, i.e. Na, K, and Ca in the raw sludge was 0.87±0.05, 0.59±0.02, and 6.40±2 % of dry solids respectively. A limited removal of the Na and K ions occurred during the treatment process (i.e. 2.3-5.7% for Na and 11.8-13.5% for K), while Ca was significantly removed (i.e. 23.4-37.3%) (Fig.4). The C/N ratio, which is an important parameter to assess total nutrient balance, was considered as one of the parameters to represent the fertilizing property of the stabilized waste-activated sludge samples (Muruganandham and Swaminathan, 2004). Thus, C/N ratio of treated sludge must be well-balanced in order to ensure its stability once applied to crop fields. Stability threshold ranges between 10 and 20 according to several studies conducted in considered wastes (Gunaseelan, 2007). In this study, C/N ratios showed a clear decrease from the raw sludge (i.e. 14.5) to treated sludge at different pH values, essentially due to the efficient total carbon (TC) removal by means of the Fered-Fenton technology. However, at pH value equals to 3, the ratio decreased to 8.47. The maximum C/N ratio, i.e. 13.7 was reached at pH value equals to 7 (Fig. 2), suggesting suitable fertilizing volatilization for agricultural land application.

3.3. Fecal coliforms removal
The spread of diseases as a consequence of using pathogenic bacteria contaminated waste sludge for agricultural land application purposes is a serious limiting factor in this regard (Aziz et al., 2013). According to the US EPA (40 CFR Part 503) regulations, Class A biosolids contain a fecal coliforms density less than 1,000 most probable number (MPN) per gram total solids (Regulations, 2003). Figure 5 shows the removal efficiency (i.e. more than 99.9%) of the investigated Fered-Fenton reactor regarding fecal coliforms and total coliforms present in the waste-activated sludge samples. The achieved results at different operating pH values equal to 3, 5, and 7 correspond to the class A requirements for sludge land application purposes. The generated hydroxyl radicals (Eq. 1) are the main affecting agent related to the inactivation of a wide range of bacteria and viruses (Daneshmand et al., 2012).
Fig. 2. Total carbon, total phosphorus, and total nitrogen content, and C/N ratio of the stabilized waste-activated sludge at different operating pH values. \([\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]=0.60\), retention time= 240 (min), \([\text{H}_2\text{O}_2]=1250\) (mg/L), current density= 600-800 (mA)

Fig. 3. Nitrate and ammonium reduction under different operating pH values \([\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]=0.60\), retention time= 240(min), \([\text{H}_2\text{O}_2]=1250\) (mg/L), current density= 600-800(mA)

Fig. 4. Micronutrients content of the stabilized waste-activated sludge samples at different operating pH values

Fig. 5. Coliforms removal efficiency of the Fered-Fenton process at different operating pH values

Initial fecal coliforms concentration in the raw WAS= 4250000 (MPN) per gram (g) total solids, initial total coliforms concentration= 40000000 (MPN) per gram (g) total solids, \([\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]=0.60\), retention time= 240(min), \([\text{H}_2\text{O}_2]=1250\) (mg/L), current density= 600-800 (mA)

Conclusions
With regard to the special importance of sludge stabilization, abundant efforts are done to find innovative solutions to optimize this stage of wastewater treatment process. In this study, considering the identified advantages and disadvantages, particularly in relation to Fenton method, it was attempted to improve the efficiency of sludge stabilization process (organic load removal) using a combined Fenton and electrochemical method. This research focused on the investigation of the Fered-Fenton process as a promising technical and environmentally friendly method of enhancing waste-activated sludge stabilization occurrence. The results have proved the high efficiency of this method in preserving the nutrients (N, P, Na, K and Ca), and reducing the fecal and total coliforms concentration. Therefore, the stabilized waste-activated sludge is suitable for agricultural land application corresponding with the US EPA regulation.
References


32
Investigation of Electro-Chemical Peroxidation (ECP) Process for Waste-activated Sludge Stabilization with the Aim of Agricultural Land Application

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Keyword: Reuse, waste-activated sludge stabilization, Electro-chemical Peroxidation (ECP), Response Surface Methodology (RSM)

Abstract

Recently, promoting the capability of waste activated sludge has been considered with the aim of improving its quality in order to be reused during its treatment processes. In this study, for the first time, the application of electrochemical peroxidation process (ECP) for wasted activated sludge stabilization and reuse in agriculture has been investigated in two steps. VSS removal efficiency has been experimentally studied in lab-scale under different operational conditions taking into consideration pH, \([\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]\), retention time and current density parameters, in the first step. Then, the optimum condition of the reactor's operation in terms of four independent parameters and designing experiments were investigated, employing the Design-Expert® software and the Central Composite Design (CCD). According to the results, the best proportion (VSS removal efficiency of 74%) of hydrogen peroxide to \(\text{Fe}^{2+}\), the optimum pH value, maximum retention time, hydrogen peroxide concentration and current density were 1.55, 3, 4 h, 1535 mg.l\(^{-1}\) and 1.17 mA.cm\(^{-2}\), respectively. Also, evaluation of the process ability for microbial coliform inactivation showed that this process is strongly reliable in eliminating microbial contamination of the sludge with a considerably high efficiency (99.9%). The results specify that electrochemical peroxidation process (ECP) can be a suitable efficient method for waste-activated sludge stabilization and reuse.

1. Introduction

Sludge management, especially waste-activated sludge stabilization and reuse, is a fundamental area of concern across the conventional wastewater treatment plants. On the other hand, this matter has various remarkable properties and is capable to be beneficially utilized as a resource of energy or useful recovered materials (Badalians Gholikandi, G, 2015). Conventional methods of sludge stabilization have several disadvantages like large quantity of sludge produced, high-energy demand, time-consuming processes, and noticeably low efficiency removing odor, pathogens, toxic organic compounds, heavy metals, and operational difficulties (Metcalf and Eddy, 2003; Turovskiy and Mathai, 2006). Thus, the growing quantity of waste sludge generated in municipal and industrial wastewater treatment plants containing various persistent organics and other contaminants stress the necessity of novel treatment technologies that are capable to achieve significant removal efficiencies under more convenient operational conditions (Badalians Gholikandi, G, 2015). Advanced treatment processes are also capable of addressing contemporary related quality issues (U.S.EPA., 2012). One of these strategies is the use of electrochemical advanced oxidation processes (EAOPs), which can remove organic contaminants with high efficiency in a short period of time (Badalians Gholikandi, G, 2015;
Concerning wastewater treatment, many of the published studies utilize an electrochemical cell with a sacrificial iron anode to produce Fe\textsuperscript{2+} via the decomposition of the anode (reaction 1) whereby H\textsubscript{2}O\textsubscript{2} is added to the solution under treatment in the final stage in order to oxidize organic materials via hydroxyl radicals (OH\textsuperscript{0}) based on the Fenton reaction (reaction 2). This process is known as Electrochemical Peroxidation Process (ECP) (Brillas et al., 2009; Neyens et al., 2003).

\begin{align*}
\text{Fe} & \rightarrow \text{Fe}^{2+} + 2e^- \\
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{OH}^0 + \text{OH}^- \quad k = 63 \text{ M}^{-1}\text{S}^{-1}
\end{align*}

In this study, according to the results of previous studies (Chiarenzelli et al., 2001; Kokkali, V., 2011; Liu et al., 2012; Ozyonar and Karagozoglu, 2015; Gutiérrez et al., 2010) and the lack of studies regarding sludge stabilization, an electrochemical peroxidation reactor in lab-scale using iron electrodes was investigated for the purpose of waste activated sludge stabilization and reuse in agriculture, taking into account of U.S.EPA guidelines (U.S.EPA., 2012). Since the parameters of retention time, [H\textsubscript{2}O\textsubscript{2}]/[Fe\textsuperscript{2+}] (ppm/ppm) ratio, pH value and electrical current have a great impact on the performance of processes based on the Fenton reaction (Badalians Gholikandi et al., 2014; Umar et al., 2010; Ismail and Tawfik, 2015), these four parameters and the extent of VSS removal were considered as input and response variables for the Design-Expert\textsuperscript{®} software, respectively.

2. Material Methods

The studied waste-activated sludge was obtained from the return sludge site at Shahid Mahalati municipal wastewater treatment plant in Tehran employing extended aeration activated sludge method. Table 1 shows the characteristics of the utilized waste activated sludge. The investigated experimental set up was made up of one liter Plexiglas cylinder containing 0.9 liter of the sludge sample fitted with four iron electrodes (Fig. 1). The 140mm × 60mm × 1mm iron electrodes were used for supplying the Fe\textsuperscript{2+} required as catalyst according to Equation 2. The depth and the aspect ratio of each electrode with sludge were 100 mm and 100mm × 60mm respectively. The distance between the electrodes in reactor was 1.5 cm (Nidheesh, and Gandhimathi, 2012). An electric motor (Zheng, zs-ri, 6(V) DC, 366 rpm) was used to provide energy for proper mixing in the system. A digital power supply (DAZHENG, DC Power, ps-305d, 0-5 A, 0-30 V) was employed to set the current and voltage consumption of the system. Hydrogen peroxide, NaOH, sulphuric acid (96%, for the pH adjustment), deionized water, and filter paper (Whatman, 42 ashless) were used. The Leauryl Trytose Broth (LTB), Brilliant Green Bile (BGB), Escherichia Coli (EC) and Plate Count Agar (PCA) cultured environments were used to study and measure the pre and post-experiment values of the sludge microbial characteristics, i.e. Coliform, total coliform, heat resistant coliforms, and heterotroph bacteria respectively. The experiments were conducted in conformity with the standard methods for the examination of water and wastewater (APHA, 1999). The results have been optimized through RSM. RSM is an important statistical technique, for designing, modeling, analyzing, and optimizing water and wastewater chemical reactions (Abdessalem et al., 2008; Barışçı and Turkay, 2015; Hammami et al., 2007). The central composite design (CCD), as the most widely applied technique was used for the optimization of the VSS removal process.
3. Results and Discussion

First, the rate of Fe introduced into the system was studied to obtain a thorough understanding of the electrodes performance under different operation conditions (Kazemirad and Badalians Gholikandi, 2016) and subsequently, the VSS removal rate of the system was investigated within a defined affective range of four parameters, i.e. (Retention time= 0-360, [H$_2$O$_2$]/[Fe$^{2+}$] ratio= 0-2, pH= 1-7, and Electrical current= 0-1000 mA).

While three of these parameters were at their minimum level (Retention time=0, [H$_2$O$_2$]/[Fe$^{2+}$] ratio=0 and Current=0), the VSS removal rate was zero. By increasing concentrations of the iron ions and hydrogen peroxide, the VSS removal efficiency of the process, showed improvement (Brillas et al., 2009). Thus, with the other three parameters set at a fixed value (pH= 3, I= 500 mA, Time= 120 min), the [H$_2$O$_2$]/[Fe$^{2+}$] ratio was the first parameter under trial investigation. According to Figure (2 a)), the VSS removal efficiency varied between 26% and 64% with an [H$_2$O$_2$]/[Fe$^{2+}$] ratio of between 0.25 and 1.5.

The catalytic performance of Fe strongly depends on the pH of the solution (Duesterberg et al., 2008). However, with an [H$_2$O$_2$]/[Fe$^{2+}$] ratio of 1.5, a Retention Time of 120 min, and an Electrical Current of 500 mA, the researchers evaluated the pH parameter. According to figure (2 a)), the ECP process exhibits its best performance in VSS removal at a pH of 3 (VSS removal efficiency = 66%), similar to most oxidation processes based on the Fenton reaction.

### Table 1: Excess sludge specification

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>pH</td>
<td>6.53-7.31</td>
</tr>
<tr>
<td>Temperature(°C)</td>
<td>13.5-15.7</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>5768-10985</td>
</tr>
<tr>
<td>VSS (mg/L)</td>
<td>3136-6682</td>
</tr>
<tr>
<td>VS (mg/L)</td>
<td>3201-6682</td>
</tr>
<tr>
<td>TS (mg/L)</td>
<td>4375-8825</td>
</tr>
<tr>
<td>TSS (mg/L)</td>
<td>4085-8537</td>
</tr>
<tr>
<td>VSS/TSS (mg/L)</td>
<td>0.76-0.78</td>
</tr>
</tbody>
</table>
Electrical current is also another important parameter in the performance of ECP processes since it affects both reduction of the Fe²⁺ ions (reaction 3) and OH⁰ production (reaction 2) (Zhang et al., 2007). According to Figure (2 b)), there was an increase in the VSS removal efficiency (to 73%) with an increase in the electrical current up to 750 mA. Then, an increase in the electrical current and the cathodic reduction of iron electrodes led to a decrease in the [H₂O₂]/[Fe²⁺] Ratio and the VSS removal efficiency (to 64%).

\[ \text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+} \]  
(3)

As demonstrated in Figure (2 b)), increasing the Retention Time to 180 min (with constant values of [H₂O₂]/[Fe²⁺] ratio= 1.5, pH= 3, and I= 750 mA) showed an increase in the VSS removal efficiency rate (to 75%). The results also proved that increasing of the Retention Time (up to 360 min) would not have any impact on the VSS removal efficiency.

Based on theoretical studies and the results of laboratory tests, a central composite design (CCD) was carried out including the minimum and maximum selected levels for A: retention time (15-360 min), B: [H₂O₂]/[Fe²⁺] ratio (0.1-2), C: initial pH (1-9), and D: DC current (100-1000 mA). Figure 3 shows the CCD experiments results for evaluation of the effect of four independent variables along with the predicted mean and observed responses (i.e., percentage of the VSS removal). Given the validity of the model and the reliability of the results provided by the RSM as presented in Figures 3(a, b) the researchers evaluated the impact of the study parameters on the removal rate more closely. The VSS removal rate rose with an increase in the Retention Time to about 180 min and an increase in the Electrical Current to 750 mA (Fig 3 (a)). However, increasing either of these parameters further have not showed any impact on the removal rate. In addition, Figure 3 (b) shows the simultaneous impact of pH and [H₂O₂]/[Fe²⁺] ratio on the system. According to this figure, an increase in pH to higher than 3.5 was associated with a tangible decrease in the VSS removal rate. Besides, an increase in the [H₂O₂]/[Fe²⁺] Ratio to 1.5 led to an increase in the removal rate. However, increasing the Ratio further was followed by decreasing in the removal efficiency. Therefore, optimum values of the study parameters were identified for optimum VSS removal. Considering the optimum operating conditions for the system (Figures 3), a VSS removal rate of 74% was obtained under laboratory conditions at the following values: Retention Time= 180 min, [H₂O₂]/[Fe²⁺] Ratio= 1.5, pH= 2.5-3.5, and Electrical Current= 750-800 mA. Also, evaluation of the microbial
characteristics results, obtained from raw and stabilized sludge in the laboratory electrochemical peroxidation system, (Table 2) showed that this system had a highly acceptable performance (99.9% efficiency) in terms of removal of microbial characteristics in the sludge. Optimum operating conditions for the system, leading to a VSS removal efficiency of 74% under laboratory circumstances showed that Electrochemical Peroxidation Process (ECP) has a very good performance in removing VSS from sludge, more comfortable operating, stability and not a function of environmental factors compared with conventional methods of sludge stabilization. Moreover, the results showed that Response Surface Modeling (RSM) is an efficient and suitable model for optimizing the system’s operating conditions. Considering the high degree of coliforms removal, the stabilized waste-active sludge was placed in Class A of the US.EPA standard (U.S.EPA., 2012). The status of its microbial characteristics makes this sludge suitable in order to be reused, particularly agricultural purpose.

Figure 3. Response surface plots of the VSS removal efficiency vs. a) the electrical current (mA), retention time (min) and b) pH, [H₂O₂]/[Fe²⁺] ratio

Table 2. Raw and stabilized sludge microbial characteristics

<table>
<thead>
<tr>
<th></th>
<th>Coliforms MPN/100ml</th>
<th>Total coliforms MPN/100ml</th>
<th>Fecal coliform MPN/100ml</th>
<th>(HPC) Cfu/0.1ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw sludge</td>
<td>8000000</td>
<td>6000000</td>
<td>1600000</td>
<td>1780000</td>
</tr>
<tr>
<td>Stabilized sludge</td>
<td>730</td>
<td>530</td>
<td>250</td>
<td>320</td>
</tr>
<tr>
<td>Growth medium</td>
<td>LTB</td>
<td>BGB</td>
<td>EC</td>
<td>PCA</td>
</tr>
<tr>
<td>Removal Efficiency (%)</td>
<td>99.9</td>
<td>99.9</td>
<td>99.9</td>
<td>99.9</td>
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</table>

References


Biogas Production from Hydrocarbon and Lipid-Spent Microalgae and Wastewater Sludge Mixtures

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Keywords: Biogas production, spent microalgae, enzymatic hydrolysis; cellulose enzymes, biofuel production, wastewater treatment sludge

Abstract

In this article, the production of biogas from hydrocarbon and lipid-spent microalgae, (\textit{Nannochloropsis Sp.}) and wastewater sludge mixtures was investigated. The spent microalgae was subjected to two treatment sequences: (1) hydrocarbons hydrolysis followed by lipid-extraction; and (2) lipid-extraction followed by hydrocarbons hydrolysis. Hydrocarbons hydrolysis was achieved using two the types of cellulose enzymes, which were compared to hydrolysis using distilled water at pH 7 or 5 or acetate buffer at pH 5. Enzymatic hydrolysis was meant to convert the hydrocarbon content of microalgae into sugars for bioethanol production and lipid extraction was meant to produce oil for biodiesel production. The results confirmed that significant quantities of biogas were generated from mixtures containing sludge and up to 50\% algae/sludge solids reaching as high as four times biogas production from sludge alone. The results also confirmed that the residual potential of algae to produce biogas declined as the effectiveness of hydrocarbons hydrolysis increased. Co-digestion of sludge and spent algae combines treatment and energy recovery from both types of residues. Furthermore, producing biogas from spent microalgae can significantly improve the feasibility of producing biodiesel and bioethanol from algae.

1. Introduction

In a relatively recent review, Brennan and Owende (2009) concluded that microalgae-derived biofuels can progressively serve as a significant substitute for fossil fuels. Scott et al. (2010) considered biodiesel production from microalgae as a milestone in developing biofuels. Biofuels from microalgae are considered promising alternatives to fossil fuels because they can reduce net CO2 emissions (Kröger and Müller-Langer, 2012) and can be produced in adequate quantities without competing with food sources. Therefore, the interest in microalgae as an attractive feedstock to produce biofuels in a sustainable manner has increased worldwide (Zhang et al. 2014; Demirbas, 2009). Microalgae can be grown using cheap nutrients, and their various species may contain high levels of lipids, hydrocarbons and proteins (Zamalloa et al., 2011). Driven by sunlight, microalgae convert CO2 and H2O into potential biofuels, foods, and other high value organic products (Walter et al., 2005).

Despite the technical feasibility of biofuel production from microalgae, the economic feasibility of the process has not yet been established. With current state of technology, Scott et al. (2010) observed that biodiesel production from microalgae may require more energy than it generates. Different strategies can be used to improve the feasibility of microalgae-based biofuels, including: anaerobic digestion of microalgae residues after lipid extraction for biodiesel
production (Torres et al., 2015); combining production of different biofuels from microalgae (Adam and Shanableh, 2016; Kaparaju et al., 2009). Researchers (Lardon et al., 2009; Torres et al., 2015; Campbell et al., 2011) have established that significant energy remains in lipid-spent microalgae, which can be recovered, for example in the form of biogas.

Of the wide variety of microalgae species, Nannochloropsis sp., which is a unicellular marine green microalga, is locally grown to feed fish in fish farms as it is known for its high lipids content and ease of growth (Rodolfi et al., 2009). Fabregas et al. (2004) reported Nannochloropsis sp. to contain approximately 60% lipids, 10% proteins, and 30% carbohydrates. Nannochloropsis microalgae has received significant attention as a source of lipid for biodiesel production, with produced biodiesel found comparable to standard biodiesel (Knothe, 2009). Other types of carbohydrates-rich microalage were considered for bioethanol production (Ho et al., 2013).

Microalgae cell walls contain low content of hemicellulose and no lignin compared to lignocellulosic biomass, which enhances extraction and production of useful resources from microalgae (Saqib et al., 2013). A variety of pre-treatment methods are available to enhance extraction of algae resources to produce biofuels, including enzymatic pretreatment, which is a promising pre-treatment alternative (Severson et al., 2012).

The main objective of this study was to evaluate the potential of producing biogas from mixtures of wastewater sludge and spent Nannochloropsis sp. microalgae subjected to enzymatic hydrolysis of hydrocarbons and lipid extraction for bioethanol and biodiesel production (Adam and Shanableh, 2016). Enzymatic pre-treatment was used for two purposes: (1) to saccharify Nannochloropsis sp. microalgae hydrocarbons; and (2) to enhance lipid extraction for biodiesel production. The residual organic matter following enzymatic treatment and lipid extraction was considered suitable as a food source for anaerobic sludge microorganisms to enhance biogas production.

2. Material Methods

The microalgae used in this study, *Nannochloropsis Sp.*, was obtained from a commercial supplier (Longevity Herbs and Superfoods, USA) and was supplied in 500 g plastic bags. The algae samples were prepared for biofuels production through washing, drying and grinding into a powder. The two enzymes used in the study were powder cellulase obtained from fungus *Trichoderma viride* (activity 3-10 units/mg), referred to herein as CTV enzyme, and liquid cellulase enzyme solution obtained from fungus *Trichoderma reesei* (700 EGU/g ~70 FPU/g), referred to herein as CTR enzyme. The two enzymes were purchased from Sigma-Aldrich, USA.

Prior to co-digestion with sludge, the microalgae was subjected to either of the following two treatment sequences, which are described below: (1) hydrocarbons hydrolysis followed by lipid-extraction using the Bligh and Dyer method (Bligh and Dyer, 1959; White et al., 1979) then followed by lipid extraction by the soxhlet extraction method; or (2) lipid extraction by the soxhlet method followed by hydrolysis of hydrocarbons. Hydrocarbons hydrolysis was achieved using either of two the types of cellulose enzymes (CTV and CTR) in an acetate buffer medium at pH 5, which were compared to hydrolysis without enzymes using distilled water at pH 7 or 5 or acetate buffer at pH 5. The microalgae samples treated using different enzyme dosages were combined and mixed together then used for biogas production.
Hydrolysis was carried out in 100 mL glass laboratory bottles. Distilled water (pH 5 or 7) or sodium acetate buffer (100 mM, pH 5) were used as a medium for hydrolysis. Hydrolysis proceeded by mixing algae (5 g for CTV or 6 g for CTR), distilled water, or acetate buffer solution, or acetate buffer solution and enzyme (0-50 mg CTV or 0-22 mL CTR) in each bottle (50 mL for CTV or 60 mL for CTR). The bottles were capped, placed inside a water bath incubator shaker (Clifton NE5-28D, UK) at the appropriate temperature (37°C for CTV, 50°C for CTR) and shaken at a speed of 300 rpm for 6 hours. It is worth mentioning that the buffer was brought to the desired hydrolysis temperatures in the incubator before adding the enzymes. After 6 hours of hydrolysis, treatment was terminated by placing the bottles in a boiling water bath at 95-100°C for 5 minutes. The contents of the bottles were then centrifuged (Centurion 8000, UK) at 6,000 rpm to separate the supernatants from the solid residues. The total sugar produced was measured using the phenol-sulfuric acid method (Dubois et al., 1956).

Lipid extraction was performed using two methods: (1) soxhlet extraction using an automatic extractor (Buchi B-811 LSV, Switzerland) with a solvent mixture consisting of methanol, chloroform and water (volume ratio of 2:1:0.8); and/or (2) extraction using the modified Bligh and Dyer method (Bligh and Dyer, 1959; White et al., 1979) with chloroform, methanol and deionized water (volume ratio of 1:2:0.8). Following hydrolysis and lipid extraction, the residual algae material was soaked in distilled water for 12 hours then oven dried and ground into powder. The hydrocarbon and lipid-spent algae was mixed with sludge samples (30 mL sludge with 2% TS) in 50 mL capped serum bottles and the pH was adjusted to approximately 7.3 then the bottles were incubated at 37°C for 16 weeks to generate biogas through anaerobic digestion. Control samples containing sludge alone were also prepared and digested. The spent algae samples were co-digested with sludge at different dry algae to sludge solids ratios in the range of 10% to 50%. Biogas production was measured periodically through inserting a hypodermic needle into the rubber stopper of the serum bottle to displace water in a U-shaped graduated manometer filled with acidified water.

3. Results and Discussion

This study is part of a research effort focused on combining the production of multiple biofuels (i.e., bioethanol, biodiesel and biogas) from microalgae (Adam and Shanableh, 2016). The spent microalgae used for biogas production in this study was subjected to two types of treatments: (1) enzymatic hydrolysis followed by lipid-extraction; and (2) lipid-extraction followed by enzymatic hydrolysis. Hydrolysis was conducted using two the types of enzymes, CTV and CTR, in addition to distilled water at pH 7 and pH 5 and acetate buffer at pH 5. Enzymatic hydrolysis was meant to convert the hydrocarbon content of microalgae into sugars for bioethanol production and to facilitate lipid extraction through disintegrating the wall structure of algae cells. The hydrocarbon content of microalgae used in this study was hydrolyzed to various degrees depending on enzyme dose used (Adam, 2016). On the other hand, lipids extraction was meant to produce oil for biodiesel production. The overall lipid content of the algae of approximately 49% was extracted prior to co-digestion of spent algae with wastewater treatment sludge.

The data in Figure 1 show the weekly biogas production from the CTV enzyme-hydrolyzed then lipid-extracted microalgae co-digested with sludge at different algae/sludge solids ratios in the range of 0-50%. The data clearly show that the quantity of biogas produced increased with time and with increased algae addition to the sludge. The data also indicate that the sample
containing sludge plus 50% algae/sludge initially lagged behind the sample containing 40% algae/sludge but eventually recovered and produced the maximum biogas quantity. Compared with sludge alone, the biogas produced from the samples containing sludge plus 50% algae/sludge was nearly three times the biogas produced from sludge alone. The results reflect the high potential of using spent microalgae for biogas production in combination with sludge. The results also confirm that the biogas generation potential of microalgae was not exhausted as a result of enzymatic treatment followed by lipid extraction.

The data in Figure 2 show the weekly biogas production from the CTR enzyme-hydrolyzed then oil-extracted microalgae. Biogas production increased with time and with increased algae addition to the sludge, with the sample containing 50% producing a maximum of 160 mL biogas, which is about 2.5 times the biogas produced from sludge alone. Compared with the microalgae samples hydrolyzed using the CTV enzyme (Figure 1), the microalgae hydrolyzed using the CTR enzyme produced significantly lower quantities of biogas (204 mL using CTV compared to 165 ml using CTR). The main difference between the CTV and CTR-hydrolyzed microalgae is the quantity of hydrolyzed hydrocarbons, which amounted to 103 and 185 mg total sugars per gram microalgae using the CTV and CTR enzymes, respectively (Adam, 2016).

To confirm the impact of enzymes on residual biogas potential of spent algae, microalgae samples were subjected to hydrolysis using water at pH 5 and 7 and using acetate buffer without enzyme at pH 5. The data show that hydrolysis using water at pH 5 or 7 or buffer produced nearly similar biogas production results, with the samples containing 50% algae/sludge producing nearly 3.5 to 4 times biogas than sludge alone. However, compared with the CTV and CTR enzymatically treated algae (Figures 1 and 2), water or acetate buffer hydrolyzed algae produced more biogas due to the higher hydrocarbon content retained in the microalgae following hydrolysis.
Figure 2. Biogas production from sludge and microalage hydrolyzed using CTR enzyme then lipid-extracted (Note: CTR=cellulase enzyme from Trichoderma reesei; LPD=lipid extracted; and AG/SG=dry algae residual/dry sludge solids)

To compare the impact of pretreatment sequence on biogas production, algae samples were prepared by first lipid extraction followed by enzymatic hydrolysis. The data in Figure 4 show biogas production from sludge mixed with lipid-extracted then CTV enzyme-hydrolyzed microalgae. The data show that biogas production reached about 3.5 times the biogas produced from sludge alone. Comparison of the two opposite treatment sequences in Figures 1 and 4 does not show significant difference in terms of total biogas production after 16 weeks of incubation, however the initial biogas production rate was higher for the lipid-extracted then hydrolyzed algae samples. Similarly, the data in Figure 5 show biogas production from the lipid-extracted then CTR enzyme-hydrolyzed microalgae. The biogas produced from samples...
containing algae reached about three times the biogas produced from sludge alone. Comparison of the two opposite treatment sequences in Figures 2 and 5 shows that biogas production from the lipid-extracted then CTR hydrolyzed algae/sludge mixtures was significantly higher than biogas production from the CTR hydrolyzed then lipid-extracted algae/sludge mixtures.

The data in Figure 6 provide comparisons of specific biogas production (i.e., ml biogas/g digested solids) after 16 weeks of incubation from mixtures of sludge and algae. The results clearly show that the addition of up to 50% of algae to sludge significantly enhanced specific biogas production by up to 2.5 times compared to sludge alone. The general specific biogas production ascending order was as follows: sludge alone; sludge with CTR enzyme-hydrolyzed...
then lipid-extracted algae; sludge with lipid-extracted then CTR enzyme-hydrolyzed algae; sludge with CTV enzyme-hydrolyzed then lipid-extracted algae; sludge with lipid-extracted then CTV enzyme-hydrolyzed algae; sludge with algae hydrolyzed with acetate buffer then lipid-extracted; and sludge with algae hydrolyzed with water (pH 7 and 5) then lipid-extracted. As the quantities of digested sludge plus algae solids were kept constant at each of the algae dosages used (10% to 50%), the differences in biogas production can be attributed to differences in the organic composition of spent algae following enzymatic hydrolysis and lipids extraction.

![Graph showing biogas production](image)

**Figure 6.** Comparison of specific biogas production after 16 weeks of incubation from the various sludge and algae mixtures and pretreatment sequences. (Note: CTV=cellulase enzyme from Trichoderma viride; CTR=cellulase enzyme from Trichoderma reesei; DW7, DW5=distilled water at pH 7 or 5; BFR5=acetate buffer at pH 5; and LPD=lipid extracted)

Lipid extraction from the spent-algae was virtually complete, however the extent of enzymatic hydrolysis of hydrocarbons to sugars varied according to the following: (1) treatment sequence; (2) effectiveness of hydrolysis, as determined by the following: use or lack of use of enzyme; type of enzyme; and pH of hydrolysis medium. The data in Figure 7 for example show the maximum total sugars produced from the different treatment sequences in relation to the quantities of biogas produced. The general trend indicates that the quantity of biogas declined as the quantity of total sugar produced through hydrolysis increased. However, the observed decline in biogas production was not proportional to the quantities of total sugars produced, which suggests that the residual organic matter in sludge, such as proteins, significantly contributed to biogas production from spent algae. Although problematic in terms of anaerobic digestion due to poor C/N ratio, and ammonia and hydrogen sulfide production, protein rich biomass was demonstrated (Kovács et al., 2013) to have a higher biogas yield potential compared to other types of biomass.
4. Summary and Conclusions

Producing biogas from hydrocarbon and lipids-spent microalgae can significantly improve the feasibility of producing biodiesel and bioethanol from algae. Furthermore, co-digestion of sludge and spent algae combines treatment and energy recovery from both types of residues. The results confirmed that significant quantities of biogas were generated from lipid-extracted and hydrocarbon-spent algae. Furthermore, the residual potential of algae to produce biogas declined as the effectiveness of hydrocarbons hydrolysis increased. Enzymatic hydrolysis significantly reduced biogas production compared to hydrolysis without enzymes. The CTR enzyme was more effective in terms of hydrolysis of hydrocarbons than the CTV enzyme and therefore reduced the biogas production potential of spent algae. On the other hand, distilled water at pH 7 was the least effective in terms of hydrolysis of hydrocarbons but the resulting spent algae produced the highest amount of biogas. The data also confirmed that hydrolysis followed by lipid extraction was more effective than lipid extraction followed by hydrolysis in terms of total sugar production but the residual algae had lower biogas production potential. Overall, the spent algae retained residual organic matter with significant biogas production potential.

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Effect of Inorganic Salt Solutions on Index Properties of Natural Liner Materials

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Keywords: landfilling, barrier systems, clay liner materials, inorganic salts, geotechnical properties

Abstract

This study presents the effect of two inorganic salts, NaCl and CaCl₂ on geotechnical properties (Atterberg Limits) of materials (clay, kaolinite and bentonite) which can be used as impermeable bottom liner in barrier systems. NaCl and CaCl₂ salt solutions were used in the experimental study to define the geotechnical characteristics of clay liner materials since the use of distilled water or tap water is far from being representative of the in-situ conditions. Results indicated that all of the salts could have a considerable effect on the index properties of the mixtures. The main reason of such effects is the changes which occur in diffuse double layer of clay particles. The behavior of the low plasticity clays is different from the high plasticity clay. The liquid limit decreases with increasing chemical concentration for high plasticity clay. The hydraulic conductivity increases with increasing chemical concentration for high plasticity clay. The effect of chemicals on the geotechnical properties may be explained by Diffuse Double Layer (DDL) and Gouy-Chapman theories. The chemical solutions tended to reduce the thickness of the DDL and flocculate the clay particles, resulting in reduction of liquid limit, reduction of swelling and increasing of hydraulic conductivity of high plasticity clays. However, the chemical solutions tended to increase the thickness of the DDL and disperse the clay particles, resulting in increasing of liquid limit, increasing of swelling and reduction of hydraulic conductivity of low plasticity clays.

1. Introduction

Geosynthetic clay liners (GCLs) and compacted clay liners (CCLs) are the most important components of landfills. The main reason in utilization of materials with low hydraulic conductivity in construction of impermeable liners is to limit or to eliminate the movement the leachate from bottom of landfills and the generated gases from the final cover. The liners are exposed to various chemical contaminants existing in landfill leachate. Consistency limits have been representative parameters to estimate clay behavior interacting with liquids (Jefferson and Rogers, 1998; Arasan and Yetimoglu, 2008). Evaluation of the consistency limits not only provides basic mechanical data about the soil but also gives a first insight into the chemical reactivity of clays. The liquid limit and plastic limit of a soil can be correlated with various engineering properties, such as permeability, shrinking and swelling behavior, shear strength, and compressibility of the soil (Sharma and Lewis, 1994; Abdullah et al., 1999; Arasan and Yetimoglu, 2008; Shariatmadari et al., 2011).
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 (Jo et al., 2005; Schmitz et al., 2004; 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 cosistency limit tests. Basically, the liquid limit, plastic limit and the plasticity index parameters are highly influenced by interaction with liquids (Schmitz et al., 2004), and the hydraulic conductivity tends to decrease when the liquid limit and the plasticity index are increased (Alawaji, 1999; Met et al, 2005; Shariatmadari et al, 2011).

The consistency limits have been representative indicators of clay behavior (Jefferson and Rogers, 1998) but variation observed in Atterberg limits regarding the effect of chemicals depends on the type of the soil. Based on experimental studies it is concluded that both the liquid limit and the plastic limit of CL clay increased when the concentration of salt solutions was increased. This increase in consistency limits could be attributed to dispersion and deflocculation of the clay particles when the clay interacted with chemicals (Arasan and Yetimoglu 2006, 2008; Rao and Mathew 1995). Additionally, salt solutions might cause to form new swelling compounds increasing the liquid limit of CL clay (Sivapullaiah and Manju, 2005). Contrasts to the findings of CL (low plasticity) clays, some researchers have indicated that the liquid limit decreased with increasing salt concentration for CH clays (Sridharan et al., 1986; Bowders and Daniel, 1987; Daniel et al., 1988; Acar and Olivieri, 1989; Edil et al., 1991; Shackelford, 1994; Gleason et al., 1997; Petrov and Rowe, 1997; Lin and Benson, 2000; Sridharan and Prakash, 2000; Schmitz et al., 2004). Reduction in liquid limit values due to increasing ion concentration can be explained with the flocculation mechanism of clay paritcles (nonswelling) and Diffuse Double Layer (DDL) theory by the authors. The electrical neutrality in dry clay is preserved by electrostatic attraction between the exchangeable cations as Mg2+, Ca2+, Na+ and K+ and the negatively charged particle surface edge. The diffuse double layer is formed when water is added to the dry clay (El-Hajji, 2006). The layer that clay particle encapsulated by water and ions is called diffuse double layer (DDL). The double layer thickness is directly proportional to the soil’s water adsorption capacity and inversely proportional to its permeability. It can be noted that an increase in the double layer thickness decreases the soil’s permeability by constricting the flow path available to the permeating liquid to travel between the soil’s particles (S. Arasan, T. Yetimoglu, 2006; Ozel,2007). It could be said that the salt solutions tends to reduce the thickness of the DDL and flocculates the CH clay particles.

Many chemicals tends to reduce the thickness of the Diffuse Double Layer (DDL), causing the soil skeleton to shrink and decrease in repulsive forces, thus promoting flocculation of clay particles, and to dehydrate interlayer zones of expandable clays (Bowders and Daniel, 1987). Concentration and valence of cations effect net electrical forces between clay mineral layers. Increasing cation concentration or cation valence result in a decrease in net repulsive forces, causing clay particles to flocculate (Sharma and Lewis, 1994). Several researchers have reported that chemical solutions at low concentrations are more effective than at high concentrations for CH clays (Gleason et al., 1997; Alawaji, 1999; Jo et al., 2001). Additionally it is reported that effects of the divalent and trivalent cations on the clays were different from those of monovalent cations (Shackelford et al., 2000, Jo et al., 2001; Kolstad et al., 2004a).
Divalent and trivalent cations were more effective than the monovalent cations from the standpoint of permeability and compressibility (Mishra et al., 2005). The thinnest double layer and the smallest swell were obtained with trivalent cations, while monovalent cations had little effect on the thickness of the double layer (Shackelford et al., 2000).

The present study was undertaken to investigate the effect of some components found in the leachate on some geotechnical properties of three different clays. Two salt solutions (Sodium Chloride (NaCl), Calcium chloride (CaCl2), and solutions) were chosen as leachate components in the tests. The tests were repeated at four different values of salt solution concentrations (0, 0.01, 0.1 and 1 N).

2. Material Methods

Three different classes (Clay, kaolinite and bentonite) of commercial clay soils were used in the tests. Materials used in this study can be classified as CH-Class (LL>50) high plasticity clay according to the Unified Soil Classification System (USCS). Index properties of the clays are given in Table 1.

<table>
<thead>
<tr>
<th>Materials</th>
<th>PL</th>
<th>LL</th>
<th>PI</th>
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<tbody>
<tr>
<td>Bentonite</td>
<td>62.5</td>
<td>487.5</td>
<td>425</td>
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<tr>
<td>Sepiolite</td>
<td>82</td>
<td>109</td>
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<tr>
<td>Kaoline</td>
<td>35</td>
<td>70</td>
<td>35</td>
</tr>
<tr>
<td>Clay</td>
<td>30</td>
<td>72</td>
<td>42</td>
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</table>

Since the leachate of the fly ash and bottom ash which is supposed to be dumped in the landfill site mostly contains ions of Na+ and Ca2+ (Ohtsubo et al. 2004; Mishra et al, 2009), solutions of NaCl and CaCl2 were chosen for this study. Solutions of 0 (i.e. DI water), 0.01, 0.1 and 1 N concentration were prepared by dissolving salt of NaCl and CaCl2 (powdered with purity grade of (95%) in DI water. Each solution was mixed in 1 L flask.

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).

3. Results and Discussion

Variation in index parameters (Liquid Limit, Plastic Limit and Plasticity Index) of liner materials (Clay, Kaolinite and Bentonite) is given Figure 1-3. It can be seen from Figure 1 that that liquid limit decreased as the NaCl and CaCl2 concentrations increased. The decrease was more significant at lower concentrations. The effect of the salt solutions on the plastic limit of CH clay is shown in Figure 2. The plastic limit increased for salt concentrations between 0.01 and 1 N.

Results of the study is found to be consistent with findings of the several researchers who have reported that chemical solutions at low concentrations are more effective than at high concentrations for CH clays (Gleason et al., 1997; Alawaji, 1999; Jo et al., 2001; Arasan and Yetimoglu, 2008). Similarly, some researchers have also indicated that the liquid limit decreased with increasing salt concentration for CH clays (Gleason et al., 1997; Schmitz et al.,
Reduction in the liquid limit of CH clay can be explained by reduction of the thickness of the DDL and flocculation of the CH clay particles due to interaction with salt solutions. Researchers also concluded that monovalent cations had less effect on the thickness of the double layer as compared with the divalent and trivalent cations (Shackelford et al., 2000; Jo et al., 2001; Kolstad et al. 2004). Similarly, the divalent and trivalent cations are more effective on permeability and compressibility of then clay materials than the monovalent cations (Mishra et al., 2005).

**Conclusion**

This study was undertaken to investigate the effect salt solutions (NaCl, CaCl2) on consistency limits of liner materials (CH class). Experimental study was performed by distilled water and salt solutions at 3 different concentrations in the range of 0.01-1 N. Results of the study showed that liquid limit and plasticity index values increased as the concentration of salt solutions increased for three different liner materials while plastic limit values decreased. The variations in consistency limits were found to be higher at low concentrations of salt solutions. Also it is determined that divalent cations had shown more significant effect than monovalent cations. It can be estimated that leachate has negative effect on geotechnical properties of CH class liner materials by decreasing the DDL thickness and increasing the hydraulic conductivity. As a result, contaminants existing in leachate migrate from leachate to groundwater more easily. It should also be pointed out that further studies on the geotechnical properties of CH clays interacted with chemicals are needed.
Figure 1 Effect of salt solutions on Likit Limit, Plastic Limit and Plasticity Index of liner materials
Phsico-Chemical, Mineralogical and Geotechnical Investigations of Natural Liner Materials

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Keywords: landfilling, natural liner materials, geotechnical properties, mineralogical properties

Abstract

The purpose of this research was to investigate the physicochemical, mineralogical and geotechnical characterization of natural liner materials (clay, kaolinite, bentonite, sepiolite) that can be used in landfilling. Geotechnical laboratory tests carried out in this research included particle analysis, specific gravity, Atterberg limits, specifically the liquid limit (LL), plastic limit (PL) and plasticity index (PI) that were used for classifying the clayey soil samples according to the Unified Soil Classification System whereas mineralogical studies performed included XRD, BET and FT-IR analyses. Results of the study showed that all materials investigated have the capability of being a liner material. Clay and kaolinite show similar properties in both mineralogical and geotechnical characterization. Physicochemically, mineralogically and geotechnically; no significant differences between four liner materials were observed except for the BET analysis. Since surface area of the materials is significantly important to adsorb the contaminants and prevent the contaminant migration through the bottom liner to groundwater, the results of the BET analysis should be taken in consideration in selection of the liner materials. Surface area of sepiolite specifically micropore area, micropore volume and macropore area and macropore volume is found to be much greater than other alternative materials.

1. Introduction

Leachates from municipal solid waste (MSW) landfills and various discarded products contain a wide mixture of chemical pollutants and constitute a potential risk to the quality of receiving water bodies, such as surface water or groundwater (Paxeus, 2000; Christensen et al., 2001; Baun et al., 2004; Oman and Junestedt, 2008; Varank et al., 2011a). Contamination of groundwater by landfill leachate represents the major environmental concern and has given rise to a number of studies in recent years (El-Fadel et al., 1997; Abu-Rukah and Al-Kofahi, 2001; Saarela, 2003; Varank et al., 2011b).

The liner system is one of the most important elements of a modern engineered landfill and soil liner generally comprising clay material is a significant component of a modern liner system. According to the Turkish Solid Waste Landfilling Regulation, the thickness of the compacted liner materials must be higher than or equal to 1 m with a hydraulic conductivity value of 10\textsuperscript{-9} m/s for sanitary landfill lining. To meet this requirement, certain characteristics of soil material should be met (Qian et al., 2002). First, the soils should contain at least 15-20\% of silt or clay-sized material. Secondly, the Plasticity Index (PI) should be in the range of 10\%-40. Thirdly,
the coarser fragments should be screened to no more than about 10% gravel-size particles (Sivapullaiah and Lakshmikantha, 2004; Arasan, 2010).

Clay liners are commonly used to limit or eliminate the movement of leachate and landfill gases from the landfill site. On the other hand, liners are exposed to various chemical, biological and physical events, and affected by complex character of the generated leachate as they are used as a barrier. To assess the durability of the liner material, it is important to study physical, chemical, geotechnical and mineralogical properties of the liner materials.

In this study basic characteristics of the liner materials (clay, kaolinite, bentonite and sepiolite) were investigated. But to use compacted inorganic materials as impermeable liners properly, more theoretical and experimental study is needed to investigate the variation of engineering properties of the materials as interacted with chemicals.

2. Materials and Methods

Physical properties of liner materials were characterized. Total solids (TS) were determined by drying a measured mass of the soil to a constant weight at 103–105 °C for 24 h whereas total volatile solids (TVS) were determined by igniting the dry solids at 550 °C for 2 h in a furnace. Results of physical and chemical characterization of the liner materials are presented as the average values for two replicates of the four samples.

The mesopore and micropore size distributions were estimated based on the Barrett–Joyner–Halenda (BJH) and Horwath–Kawazoe (HK) theory, respectively. The Brunauer–Emmet–Teller (BET) surface areas and BJH pore distributions were determined using the Quantachrome Ins. Quadrasorb SI model instrument by the nitrogen adsorption at 77 K. The specific surface area was calculated based on the BET equation. The micropore surface area and volume were calculated by the t-method. X-ray diffraction (XRD) measurements were performed on a X-ray diffractometer using CuKα radiation. Qualitative estimation of the surface functional groups was performed by the Fourier transform infra-red spectroscopy (Perkin Elmer Spectrum 100 Model) by the potassium bromide (KBr) pellet method.

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).

3. Results and Discussion

Physico-Chemical characteristics of natural liner materials are given in Table 1 and index parameters of the liner materials are given in Table 2. As can be seen from Table 2, that bentonite, clay and kaolinite can be classified as CH-Class (LL>50) high plasticity clay whereas sepiolite can be classified as CL-Class (LL<50) low plasticity clay according to the Unified Soil Classification System (USCS). Bentonite has very high LL and PI values as compared with the other liner materials. Soils with very high PI, are sticky and are difficult to work with. Also high PI soils form hard clumps when the soils are dry and difficult to break down during compaction.
Table 1. Physico-Chemical characteristics of natural liner materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>pH</th>
<th>Conductivity (μS/cm)</th>
<th>Water content (%)</th>
<th>TS (%)</th>
<th>Organic Matter Content (%) (TVS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bentonite</td>
<td>10.14</td>
<td>0.52</td>
<td>0.096</td>
<td>90.4</td>
<td>0.02</td>
</tr>
<tr>
<td>Sepiolite</td>
<td>9.0</td>
<td>1.56</td>
<td>0.06</td>
<td>94</td>
<td>0.04</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>8.21</td>
<td>3.23</td>
<td>0.016</td>
<td>98.4</td>
<td>0.10</td>
</tr>
<tr>
<td>Clay</td>
<td>5.37</td>
<td>0.83</td>
<td>0.04</td>
<td>96</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Table 2. Atterberg Limits of natural liner materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>PL</th>
<th>LL</th>
<th>PI</th>
<th>Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bentonite</td>
<td>62.5</td>
<td>487.5</td>
<td>425</td>
<td>CH</td>
</tr>
<tr>
<td>Sepiolite</td>
<td>82</td>
<td>109</td>
<td>27</td>
<td>CL</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>35</td>
<td>70</td>
<td>35</td>
<td>CH</td>
</tr>
<tr>
<td>Clay</td>
<td>30</td>
<td>72</td>
<td>42</td>
<td>CH</td>
</tr>
</tbody>
</table>

XRD analysis provides a look into the extent of clay crystallization and in some cases a clue as to the organic incorporation (Dogan et al., 2008) and gives chemical composition of the soil materials. The characteristic XRD peaks for the liner materials are shown in Table 3. As seen from Table 3 that clay and kaolinite showed similar chemical characteristics. The constituents of the samples were determined, and identified as major (mj), minor (mi) and trace (t) amounts. XRD analysis showed that bentonite, kaolinite and clay samples contained mainly quartz whereas the main constituent of sepiolite samples was dolomite.

Table 3. The results of XRD analysis of natural liner materials

<table>
<thead>
<tr>
<th>Bentonite</th>
<th>Sepiolite</th>
<th>Kaolinite</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>sodium</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>beldelite</td>
<td>sanidine</td>
<td>quartz</td>
<td>quartz</td>
</tr>
<tr>
<td>silicon</td>
<td>orthoclase</td>
<td>kaolinit</td>
<td>kaolinit</td>
</tr>
<tr>
<td>oxide</td>
<td>dolomite</td>
<td>alunite</td>
<td>illit</td>
</tr>
<tr>
<td>cobalt</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>iron</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>vanadium</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>oxide</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The results of BET analysis of natural liner materials are given in Table 4. It can be seen from Table 4 that surface area (including mesopores and macropores area) of sepiolite was found to be the highest and the values of surface area of clay and kaolinite were determined to be very close to each other. Bentonite and sepiolite had macroporous structure whereas clay and kaolinite had mesoporous structure.

Although the information obtained from FT-IR scanning was limited as the concentrations of the functional groups on the sample surface were in fact very low, the absorption spectra
provide the evidence of the presence of some surface functional groups. The main absorption peaks and the attribution of liner materials are given Figure 2. FTIR spectra of the liner materials were recorded in the region 4000–650 cm\(^{-1}\).

<table>
<thead>
<tr>
<th>Materials</th>
<th>Surface area (m(^2)/gr)</th>
<th>Mikro-pore area (m(^2)/gr)</th>
<th>Mikro-pore volume (cc/Å/gr)</th>
<th>Mikro-pore diameter (Å)</th>
<th>Makro-pore area (m(^2)/gr)</th>
<th>Makro-pore volume (cc/Å/gr)</th>
<th>Makro-pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bentonite</td>
<td>48.537</td>
<td>22.17</td>
<td>0.045</td>
<td>1.030e+ 01</td>
<td>26.367</td>
<td>0.095</td>
<td>16.038</td>
</tr>
<tr>
<td>Sepiolite</td>
<td>106.374</td>
<td>42.983</td>
<td>0.042</td>
<td>8.800e+ 00</td>
<td>63.391</td>
<td>0.337</td>
<td>16.043</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>27.315</td>
<td>5.266</td>
<td>0.006</td>
<td>8.800e+ 00</td>
<td>22.049</td>
<td>0.120</td>
<td>19.483</td>
</tr>
<tr>
<td>Clay</td>
<td>27.142</td>
<td>8.693</td>
<td>0.009</td>
<td>8.800e+ 00</td>
<td>18.449</td>
<td>0.035</td>
<td>19.329</td>
</tr>
</tbody>
</table>

The results of BET analysis of natural liner materials

The characterization bands of bentonite (Figure 2) that appeared at 3416–3627 cm\(^{-1}\) as assigned to OH stretching vibrations which may arise from the isomorphic substitution in the tetra and octahedral layers in bentonite (Alkaram et al., 2009). The characteristic IR bands of Al and Mg bound water molecule appeared at 1634 cm\(^{-1}\). The band at 1634 cm\(^{-1}\) corresponds to the OH deformation of water. A weak band at around 1430 cm\(^{-1}\) indicates presence of carbonate bearing minerals in the sample. The peak which characterized Al–OH bendings is represented by the bands at 1116 cm\(^{-1}\). Also the bands from 711 to 882 cm\(^{-1}\) are the most characteristic for quartz.

The broad and flat band at 3604 -3297 cm\(^{-1}\) observed at the FTIR spectrum of the sepiolite could be assigned to hydroxyl groups probably attributed to adsorbed water. A weak band at around 1472 cm\(^{-1}\) indicates presence of carbonate bearing minerals in the sample. The main band in the FT-IR spectra of sewage sludge in the region 1200–900 cm\(^{-1}\) was assigned to Si–O–Si structures associated with pronounced concentration of silicon in the sample. C–H structures originating from aromatic compounds manifesting with 650–900 cm\(^{-1}\) bands can also be observed at materials’ surface.

It can be seen from FTIR spectrum kaolinite and clay that both materials showed similar IR spectra. FTIR band assignments of clay and kaolinite are given in Table 5. The results of FTIR are quite helpful in the identification of various forms of minerals present in the materials. IR spectra of clay and kaolinite showed band at 3650-3700 cm\(^{-1}\) of corresponding to H2O vibrations, indicating the hydrous nature of these materials and the presence of hydroxyl linkage. The appearance of (Si–O–Si) vibrations and (Si–O) stretch bands also support the presence of quartz. Different from kaolinite, a band at 1634cm–1 in the spectrum of clay suggests the possibility of water of hydration in the material. The inter layer hydrogen bonding in clay and kaolinite is assigned by a characteristics band at 3621 cm–1. Most of the bands such as 3694 cm\(^{-1}\), 3692 cm\(^{-1}\), 3621 cm\(^{-1}\), 111 cm\(^{-1}\), 1114 cm\(^{-1}\), 1026 cm\(^{-1}\), 1022 cm\(^{-1}\), 911 cm\(^{-1}\), 909 cm\(^{-1}\), 795 cm\(^{-1}\), 691 cm\(^{-1}\) show the presence of kaolinite (Tuddenham and Lyon 1960). The presence of bands at 3694 cm\(^{-1}\), 3692 cm\(^{-1}\), 3621 cm\(^{-1}\), 1634 cm\(^{-1}\), 1026 cm\(^{-1}\), 1022 cm\(^{-1}\), 911 cm\(^{-1}\), 909 cm\(^{-1}\) and 795 cm\(^{-1}\) indicate the possibility of the presence of illite whereas 3621 cm\(^{-1}\), 1634 cm\(^{-1}\), 1021 cm\(^{-1}\), 1026 cm\(^{-1}\) are indicative of gypsum. A shoulder at 1160 cm\(^{-1}\) indicates presence of quartz. The spectral region between 800 and 750 cm\(^{-1}\) is very sensitive against the
crystallinity and the purity of the kaolinite mineral. Pure kaolinite exhibits two peaks (795 cm\(^{-1}\) and 754 cm\(^{-1}\)) in this region.

![Figure 2. The results of FT-IR analysis of natural liner materials](image)

<table>
<thead>
<tr>
<th>Clay</th>
<th>Kaolinite</th>
<th>Assignment</th>
<th>Clay</th>
<th>Kaolinite</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band (cm(^{-1}))</td>
<td>Band (cm(^{-1}))</td>
<td></td>
<td>Band (cm(^{-1}))</td>
<td>Band (cm(^{-1}))</td>
<td></td>
</tr>
<tr>
<td>3694</td>
<td>3692</td>
<td>OH vibration</td>
<td>1021</td>
<td>1026</td>
<td>Si-O(^{2-})</td>
</tr>
<tr>
<td>3621</td>
<td>3621</td>
<td>OH vibration</td>
<td>995</td>
<td>1003</td>
<td>Si-O(^{2-})</td>
</tr>
<tr>
<td>3653</td>
<td>3650</td>
<td>OH vibration</td>
<td>909</td>
<td>911, 934</td>
<td>Al-(\cdots)-O-H</td>
</tr>
<tr>
<td>1163</td>
<td>1166</td>
<td>Al-OH</td>
<td>794</td>
<td>795</td>
<td>Si-O-Si</td>
</tr>
<tr>
<td>1111</td>
<td>1113</td>
<td>Si-O-Si</td>
<td>692</td>
<td>691</td>
<td>Si-O</td>
</tr>
</tbody>
</table>

**Conclusion**

In this study, the physicochemical, mineralogical and geotechnical properties of natural liner materials (clay, kaolinite, bentonite, sepiolite) that can be used as alternative liner materials in sanitary landfilling were investigated. Results of the study showed that no significant difference was observed in physico-chemical properties of the materials. Bentonite, clay and kaolinite can be classified as CH-Class (LL>50) high plasticity clay whereas sepiolite can be classified as CL-Class (LL<50) low plasticity clay according to the Unified Soil Classification System (USCS). Due to BET analysis, surface area (including mesopores and macropores area) of sepiolite was found to be highest and this can be associated with the highest adsorption capacity. Results of the XRD analysis showed that clay and kaolinite were similar properties in chemical characterization. Bentonite, kaolinite and clay samples contain mainly quartz whereas the main constituent of sepiolite samples was dolomite. XRD analysis results were supported by FTIR scanning. Consequently, bentonite has very high PI values and soils with very high PI values
are not appropriate to be used as a liner material because of being sticky and difficult to work with. Other natural materials can be utilized as liner materials in sanitary landfills as evaluated according to the physicochemical, mineralogical and geotechnical properties but further detailed study is needed.

References


Reduction and Biogas Recovery during Anaerobic Digestion of the X-Ray Contrast Agent Iopamidol

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Keywords: Anaerobic Digestion, Biogas Recovery, Iopamidol, X-Ray Contrast Media

Abstract

The objective of this study was to investigate the removal of the micropollutant and X-ray contrast medium Iopamidol (IOPA) and its effect on biogas recovery during anaerobic digestion in lab-scale batch reactors treating synthetic domestic sewage. Initial total COD (COD_{tot}) concentrations varied between 800-950 mg/L in the batch reactors having IOPA concentrations between 0-100 mg/L. Results of this study reflected that IOPA concentrations up to 100 mg/L did not result in any significant decrease in the anaerobic treatment performance based on COD removal and biogas production. Although the highest total and soluble COD removals were observed in the reactor having no IOPA (i.e., 77% COD_{tot} and 90% COD_{sol}); no meaningful change was observed at increased IOPA concentrations from 25 to 100 mg/L. Results also indicated that IOPA could be removed from the supernatant at a rate by 33-44% in batch reactors at the end of the incubation period. Moreover, maximum cumulative biogas production was observed as 134 mL CH₄ in the reactor with 75 mg/L IOPA compared to 111 mL in the control system with no IOPA.

1. Introduction

The presence of high concentrations of pharmaceutical residuals in the aquatic environment, sludge, soils and sediments has gained considerable attention and concern in the recent past. Among the pharmaceuticals being frequently encountered in aquatic ecosystems; iodinated X-ray contrast media (ICM) are chemicals used to enhance the imaging of organs or blood vessels during diagnostic tests (Seitz et al., 2006). Iopamidol (IOPA; C₁₇H₂₂I₃N₃O₈; 777 g/mol) is the widely used ICM and concentrations up to 2.7, 15, 2.4, and 0.49 µg/L have been detected in raw water, in treated sewage, in groundwater and in rivers, respectively (Ternes and Hirsch, 2000). It may also undergo transformation to halogenated disinfection byproducts in water treatment system (Wendel et al., 2014). ICM belong to the most frequently applied compounds in medicine They exhibit a high polarity and are very persistent against metabolism by the organism and environmental degradation (Hirsch et al., 2000). Pharmaceutical compounds are not sufficiently removed at conventional water and wastewater treatment plants due to their persistence and high degree of dilution. It has also been also reported that the removal of these compounds from water sources is difficult due to their hydrophilic nature. Conventional wastewater treatment processes have limited elimination capacities as they are not specifically designed to remove pharmaceuticals from wastewater. Some persistent substances (i.e., diclofenac, sulfamethoxazole, trimethoprim, carbamazepine) have not been significantly transformed (<25%) by the biological treatment (Suárez et al., 2010). Hence, they may form a threat to aquatic life and in the worst case may re-enter the water cycle when discharged to
surface waters (Luo et al., 2014). Ternes and Hirsch (2000) detected iopamidol, diatrizoate, iothalamic acid, ioxithalamic acid, iomeprol, and iopromide at almost the same levels in influents and effluents of municipal WWTP. Seven wastewater treatment facilities in Texas, Arizona and California were studied and organic iodine concentrations at these facilities varied between 5 and 40 µg/L (Drewes et al., 2001). Moreover, McArdell et al (2010) performed an occurrence study investigating 69 common pharmaceuticals that can be expected in the effluent of medical facilities. They reported that 52 of them were detected with IOPA being at the highest concentration in the mg/L range. Machek Jr. (2015) reported that the relatively inert ICM are found in high concentrations in clinical and domestic wastewater, surface waters, groundwater, back filtrate, soil leachates, and even drinking water supplies. Concentrations in the hospital wastewater thus correlate with the daily consumption in the hospital reaching up to 384 g/d for IOPA (Weissbrodt et al., 2009). Concentrations range from 72 to 78,000 ng/l in surface water and from 810 to 680,000 ng/l in treated wastewater (Zemann et al., 2015).

Verlicchi et al. (2012) reported that in conventional wastewater treatment plants; there are two mechanisms that play a significant role in the removal of pharmaceuticals; (i) Biodegradation/biotransformation and (ii) Sorption to solids wasted as the sludge. Due to their hydrophobic characteristics; many pharmaceutical chemicals are adsorbed by the sludge produced at primary and secondary sedimentation tanks at WWTPs. Sorption of these chemicals onto sludge relies on the physical-chemical properties of these chemicals such as their lipophilic or acidic characteristics. Pharmaceutical chemicals may; (i) sorb onto bacterial lipids by hydrophobic interactions (aliphatic and aromatic groups), (ii) be adsorbed onto the negatively loaded polysaccharides of the bacterial cells by electrostatic interactions, or (iii) are chemically bounded on bacterial proteins and nucleic acid compounds (Meakins et al., 1994). Lin and Gan (2011) demonstrated that diclofenac-like pharmaceuticals are poorly adsorbed on solid particles at anaerobic conditions and its anaerobic treatment indicated that this chemical could be removed from the supernatant in the range of 30-50% while the rest remains in the liquid phase without any abatement. Diclofenac was transmitted to sludge phase less than 10% (Okutman-Tas, 2014). Martin et al. (2015) studied the occurrence of pharmaceutical compounds in seven types of sewage sludge from different sludge treatments during one-year period. The evolution of the pharmaceutical concentrations alongside sludge treatments was characterized by a decrease from primary, secondary or mixed sludge to anaerobically or aerobically-digested sludge and by a slight increase after composting. A higher decrease was observed after anaerobic digestion due to higher degradation of these chemicals under anaerobic conditions. Several processes were investigated for ICM removal from the clinical wastewater. Biologically activated membranes were able to reduce pharmaceuticals to a concentration of 20% or less; however, ICM showed lower removal efficiencies, approximately 100% of the initial IOPA remained in solution after treatment (McArdell et al., 2010). The results of this research showed that ionic ICM like diatrizoate was not susceptible to microbial transformation, but nonionic ICM like iohexol, iomeprol and iopamidol, were capable of being transformed by microbial degradation (Kormos et al., 2010). Advanced oxidation processes and ozonation also proved to be ineffective at removal of the ICM.

The objective of this study was to investigate the reduction of the commercially important iodinated organic X-ray contrast medium IOPA and its effect on biogas recovery during anaerobic digestion in lab-scale batch reactors treating synthetic domestic sewage. Inhibition of the anaerobic treatment was evaluated on the basis of, cumulative biogas production and
other conventional parameters used in anaerobic treatability studies. Considering the gap in the scientific literature, in the present work the degradation of aqueous IOPA (25-100 mg/L) under anaerobic conditions at mesophilic temperature (35°C) was examined in synthetic domestic wastewater. Experiments were also conducted without the presence of IOPA. Critical process variables including IOPA, total and soluble COD, total and volatile solids concentrations as well as biogas productions in batch reactors were followed during anaerobic treatment of IOPA.

2. Material Methods

IOPA (1,3-Benzenedicarboxamide, N,N’-bis[2-hydroxy-1-(hydroxymethyl)etyl]-5-[(2-hydroxy-1-oxopropyl)amino]-2,4,6-triiodo-, (S); C_{17}H_{22}I_3N_3O_8; 777 g/mol; CAS: 0060166-93-0) is a non-ionic radiographic contrast agent commercially available as “Pamiray 300/370” solution. Pamiray solution was purchased from BIEM Pharmaceutical Co. A.S. (Ankara, Turkey). According to the manufacturer, 1 mL “Pamiray 300” solution contains 612.4 mg IOPA equivalents to 300 mg iodine. The other ingredients are excipients are trometamole (tromethamine), disodium calcium edetate, diluted hydrochloric acide and distilled water.

Anaerobic digestion experiments were conducted with N\textsubscript{2}-flushed, 1 L glass flasks (i.e., two parallel reactors) incubated at 35°C and they were stirred twice a day manually. The inoculum was taken from mesophilic anaerobic digester treating municipal sludge. Control reactors were also run in parallel to the sample reactors with the addition of the seed (150 mL) and synthetic sewage samples (500 mL). The high strength synthetic sewage was prepared according to the OECD guidelines [i.e., in each litre of tap water; 3 fold of the following chemicals were dissolved: Peptone, 160 mg; meat extract, 110 mg; urea, 30 mg; anhydrous dipotassium hydrogen phosphate (K\textsubscript{2}HPO\textsubscript{4}), 28 mg; sodium chloride (NaCl), 7 mg; calcium chloride dihydrate (CaCl\textsubscript{2}.2H\textsubscript{2}O), 4 mg; magnesium sulphate heptahydrate (Mg\textsubscript{2}SO\textsubscript{4}.7H\textsubscript{2}O), 2 mg]. Accordingly, initial COD\textsubscript{tot} concentration of the IOPA free control reactor was measured about 800 mg/L. All reactors were setup by the introduction of IOPA with the following concentrations; 0 (control), 25, 50, 75, 100 mg/L. Such IOPA concentrations were selected in order to examine the extent and the time that biogas productions continued and inhibition was observed.

Total COD (COD\textsubscript{tot}), Soluble COD (COD\textsubscript{sol}), Total Solids (TS), Total Volatile Solids (TVS), Suspended Solids (SS), Volatile Suspended Solids (VSS), pH, and alkalinity parameters were measured at the beginning and end of the incubation period according to Standard Methods (APHA, 2005). The changes in IOPA concentrations at the end of the anaerobic digestion experiments were quantified on an Agilent 1100 Series HPLC equipped with a Diode-Array Detector (DAD; G1315A, Agilent Series) set at 242 nm. The C18 Symmetry (Waters, USA) column (3.9 mm × 150 mm) was utilized as a stationary phase, while the mobile phase was a mixture of acetonitrile/water in 10/90 (v/v) ratio. The flow rate was set at 1.0 mL/min and the temperature of the column was set at 25°C. The quantification limit of IOPA for an injection volume of 100 µL was calculated as 10 times of the signal-to-noise ratio (3.34 µg/L). Additionally, total gas productions during anaerobic digestion were daily monitored using Lutron PM-9107 manometer. All the reactors were operated in batch-mode for 32 days until changes in the cumulative biogas production volumes were negligible and stopped after approximately a month.
3. Results and Discussion

The effect of IOPA on biogas recovery during anaerobic digestion was investigated in lab-scale batch reactors treating synthetic domestic sewage. Experiments were conducted without and with the presence of IOPA (25-100mg/L). Results indicated that IOPA concentrations in the range of 25-100 mg/L did not result in any substantial decrease in the anaerobic treatment performance based on COD removal and biogas production (Table 1). The initial pH and alkalinity of the substrate was about 7.9 and 490 mg CaCO₃/L, respectively. At the end of the anaerobic treatment, the pH values of the reactors decreased to between 7.2-7.4; however, no inhibition related to the pH changes was observed. Initial TS and TSS concentrations were about 5000 and 3775 mg/L respectively with a volatile content of ca. 50%. Although the highest COD removals were observed in the reactor having no IOPA (i.e., 77% CODₜₒₜ and 90% CODₜₒₜ); no meaningful change was observed at the investigated IOPA concentrations. CODₜₒₜ removals for different initial IOPA concentrations are presented in Figure 1a. According to Figure 1a, CODₜₒₜ removals were in the range of 70-74% in the batch reactors with the presence of IOPA. Results also indicated that this X-ray contrast agent could be removed from the supernatant with a ratio of 33-44% at batch reactors at the end of the incubation period of 32 days (Figure 1b).

<table>
<thead>
<tr>
<th>Incubation Time (day)</th>
<th>Parameter</th>
<th>Unit</th>
<th>0 (Control)</th>
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<th>75</th>
<th>100</th>
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<tbody>
<tr>
<td>0</td>
<td>CODₜₒₜ</td>
<td>mg/L</td>
<td>803</td>
<td>837</td>
<td>871</td>
<td>905</td>
<td>940</td>
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<tr>
<td>32</td>
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<td>77</td>
<td>73</td>
<td>74</td>
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<td>72</td>
</tr>
<tr>
<td>0</td>
<td>CODₜₒₜ</td>
<td>mg/L</td>
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<td>737</td>
<td>772</td>
<td>806</td>
<td>840</td>
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<tr>
<td>32</td>
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<td>85</td>
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<tr>
<td>0</td>
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<td>mg/L</td>
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<td>4825</td>
<td>4405</td>
<td>4660</td>
<td>4455</td>
</tr>
<tr>
<td>32</td>
<td>VS</td>
<td>mg/L</td>
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<td>2215</td>
<td>1915</td>
<td>2125</td>
<td>1965</td>
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<tr>
<td>0</td>
<td>TSS</td>
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<tr>
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<tr>
<td>0</td>
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<td>50.25</td>
<td>67.50</td>
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</table>

The elimination of IOPA during anaerobic digestion might not only depend on its biodegradation but also on its ability to sorb onto solid particles. It was reported that sewage sludge tends to concentrate potential contaminants from wastewater such as pesticides, metals, pharmaceutically active compounds and other organic chemical residues. These compounds are called “emerging pollutants” in the last decade, not only due to their potential ecotoxicological risks, but also to their continuous discharge to the environment (Hernando et al., 2006; Clarke and Smith, 2011; Verlicchi et al., 2012).

Biogas production also continued as the IOPA concentration in the batch systems increased from 0 to 100 mg/L. Maximum cumulative biogas production was observed in the reactor having 75 mg/L IOPA concentration (i.e. 134 mL) compared to control system (i.e. 111 mL) as...
shown in Figure 3 corresponding to 22% increase. However, biogas production relative to the control was not substantially different in lab-scale batch reactors treating synthetic domestic sewage with the presence of IOPA (25-100 mg/L).

Figure 1. Profiles of (a) CODtot and (b) IOPA at increasing IOPA concentrations during anaerobic digestion [IOPA=25-100 mg/L; T=35°C; Digestion Time=32 days]

Figure 1. Biogas productions at varying IOPA concentrations in anaerobic batch reactors incubated at 35°C. [IOPA=0, 25, 75, 100 mg/L; T=35°C; Digestion Time=32 days; Initial CODtot = 800-950 mg/L]

Conclusions

In the present study the effect of the commercially important X-ray contrast agent IOPA on anaerobic treatment performance in batch reactors was examined. The following conclusions could be made from the experimental findings;

1. Results indicated that IOPA concentrations in the range of 25-100 mg/L did not result in any substantial decrease in the anaerobic treatment performance based on COD removal and biogas production.

2. Initial CODtot and CODsol concentrations of the IOPA free control reactor were about 800 and 700 mg/L, respectively. Although the highest COD removal was observed in the IOPA free control reactor (i.e., 77% CODtot and 90% CODsol); no meaningful change was observed at increased IOPA concentrations.

3. CODtot removals were in the range of 70-77% in the batch reactors without and with the presence of IOPA.
4. Cumulative biogas productions in the reactors with IOPA concentrations up to 100 mg/L was not substantially different (99-134 mL) relative to the control (111 mL) reactor.
5. The investigated X-ray contrast agent IOPA (25-100 mg/L) could be removed from the supernatant with a ratio of 33-44% at batch reactors at the end of 32-day anaerobic digestion.

It is recommended that IOPA should be also measured in the sludge phase in future studies in order to evaluate whether its reduction in the supernatant was due to microbial removal or sorption onto solid particles.

References


Enhanced Degradation of Micropollutants by Zero Valent Aluminum Activated Persulfate: Assessment of Toxicity and Genotoxic Activity


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Keywords: Octylphenol polyethoxylate, Iodinated X-ray contrast media, Antibiotics, Bisphenol A, nanoscale zero valent aluminum, acute toxicity and genotoxicity.

Abstract

Activation of persulfate (PS) with zero valent aluminum (ZVAl) nanoparticles was investigated for the treatment of 2 mg/L aqueous octylphenol ethoxylate (OPEO), iopamidol (IOPA), ciprofloxacin (CIP) and Bisphenol A (BPA) at 1 g/L ZVAl concentration and pH 3 for 120 min. In order to investigate the effect of water constituents, the selected micropollutants (MPs) were treated in real surface water (RSW) and distilled water (DW). Two different standard acute toxicity tests using *Vibrio fischeri* and *Pseudokirchniella subcapitata* as well as the UMU-Chromo genotoxity test were performed to evaluate the ecotoxicological effects of the selected MPs and their degradation products in DW and RSW. PS could be activated with ZVAl resulting in a dramatic enhancement of MPs degradation due to the enhancement of sulfate radicals (SO$_4^{•-}$) generation. OPEO and CIP were completely degraded after 90 and 120 min treatment with ZVAl/PS in DW whereas 94% IOPA and 98% BPA removals were achieved after 120 min. MPs degradation rates were considerably retarded in RSW sample owing to the presence of organic and inorganic competitors for SO$_4^{•-}$. The corresponding OPEO, IOPA, CIP and BPA removal efficiencies in RSW were 59%, 29%, 73% and 46%, respectively. *Vibrio fischeri* and *Pseudokirchneriella subcapitata* acute toxicity tests exhibited a fluctuating trend throughout the ZVAl/PS treatment depending on the sensitivity of the test organism and the nature water matrix. ZVAl/PS treatment of OPEO, IOPA and BPA in DW did not result in cytotoxic and genotoxic degradation products, whereas CIP oxidation ended up in degradation products with genotoxic effects after 120 min ZVAl/PS treatment.

1. Introduction

In the past decades, the presence of micropollutants (MPs) in water sources has raised considerable attention due to their potential harmful environmental and health impacts. The MP group includes a wide variety of compounds such as pharmaceuticals, personal care products, hormones, industrial additives and household chemicals. The main sources of MPs are wastewater treatment plants for domestic sewage, wastewater from hospital effluents, chemical manufacturing plants, livestock and agriculture. Major consequences of MPs are: feminization of higher organisms, microbiological resistance and accumulation in soil, plants and animals, short-term and long-term toxicity, endocrine-disrupting effects, and antibiotic resistance of microorganisms (Fent et al., 2006). It is unlikely that the conventional treatment of wastewater or water will be able to remove MPs due to their chemical stability and low biodegradability (Gavrilescu et al., 2015). Advanced oxidation processes (AOPs), characterised by the generation of highly reactive, non-selective free radicals such as sulfate (SO$_4^{•-}$, $E^0 = 2.6$ V) and hydroxyl (HO$, E^0 = 2.7$ V), offer a promising alternative to
conventional treatment for the removal of MPs in water or wastewater. In the past years, peroxodisulfate (PS, $\text{S}_2\text{O}_8^{2-}$) has attracted increasing attention in AOPs applications since it is much more stable than hydrogen peroxide. Upon thermal, chemical or photochemical activation, it is possible to generate $\text{SO}_4^{\bullet-}$ from PS (Antoniou et al., 2010). The activation of PS with nanoscale zero valent iron (ZVI) and aluminum (ZVAl) to generate $\text{SO}_4^{\bullet-}$ has exhibited a great potential in the oxidative treatment of refractory contaminants (Arslan-Alaton et al., 2016a, b; Girit et al., 2015). ZVAl/H$^+$/O$_2$ treatment system (at pH<4 and in the presence of O$_2$) involves two major processes, the corrosive dissolution of Al$^{3+}$ and simultaneous reduction of O$_2$ to hydroperoxyl radical(s), HO$_2^{\bullet}$, leading the formation of H$_2$O$_2$ and generation of HO$^{\bullet}$ by an electron transfer mechanism from ZVAl to H$_2$O$_2$;

$$\text{Al}^0 \rightarrow \text{Al}^{3+} + 3e^- \quad (1)$$
$$\text{O}_2 + H^+ + e^- \rightarrow \text{HO}_2^{\bullet} \quad (2)$$
$$2\text{HO}_2^{\bullet} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (3)$$
$$\text{Al}^0 + 3\text{HO}_2 \rightarrow \text{Al}^{3+} + 3\text{HO}^\bullet + 3\text{OH}^- \quad (4)$$

The addition of oxidants substantially improve the treatment efficiency of organic pollutants (Arslan-Alaton et al., 2016a, b; Girit et al., 2015) due to the direct electron transfer from the Al$^0$ surface to the PS under acidic pH conditions;

$$2\text{Al}^0 + \text{S}_2\text{O}_8^{2-} + 6\text{H}^+ + 1.5\text{O}_2 \rightarrow 2\text{Al}^{3+} + 2\text{SO}_4^{\bullet-} + 3\text{H}_2\text{O} \quad (5)$$

During the application of AOPs, the main concern relates to the formation of various degradation products that can potentially be more toxic, estrogenic, teratogenic, mutagenic, carcinogenic, genotoxic and/or persistent than the original compound/pollutant. In addition, the natural water matrices may change the degradation products formed during the application of AOPs, which in turn may lead to different levels of biological activity depending on the variability in the water quality characteristics. Thus bioanalytical tools are necessary to examine the impact of individual MPs and their degradation products but also the effects exerted by water/wastewater as a whole (Papa et al., 2016). Among the variety of bio-analytical tools currently studied a set of bioassays representing different modes of toxic action such as estrogenicity, genotoxicity, together with baseline toxicity tests must be conducted for ecotoxicological assessment.

In the present work, PS activation with ZVAl (ZVAl/PS) for the removal of MPs in distilled water (DW) and raw surface water (RSW) spiked with MPs was investigated. Four extensively used chemicals that enter the aquatic environment through different discharge routes and ultimately form MPs were selected: the potentially endocrine disrupting compound Bisphenol A (BPA), an octylyphenol ethoxylate-based surfactant (OPEO), the iodinated X-ray contrast media Iopamidol (IOPA) and the fluoroquinolone type antibiotic ciprofloxacin (CIP). Treatment performance was assessed in terms of target pollutant removals. The ecotoxicological effects were measured on two target organisms: Vibrio fischeri (V. fischeri) and Pseudokirchneriella subcapitata (P. subcapitata) in order to focus on taxa playing a different role in the trophic web (primary producer and decomposer, respectively). Besides, the Umu-Chromo test was employed to assess the genotoxic activity of untreated and ZVAl/PS-treated effluents.
2. Materials and Methods

Materials
Commercial-grade ZVAl nanoparticles (BET surface area: 10-20 m²/g; particle size: 100 nm; purity: >99.9%) were purchased from US Research Nanomaterials, Inc. (Houston, USA). TX-45 ((C₅H₅O)₆C₁₅H₂₅O; CAS No: 9002-93-1; purity: 98%) was purchased Merck (Germany). TX-45 has an average ethoxylate chain length of approximately five. IOPA (777 g/mol; C₁₁H₂₂I₃N₃O₈; CAS No: 60166-93-0) is a non-ionic radiographic contrast agent commercially available as “Pamiray 300/370” injectable solution. IOPA was purchased from BIEM Pharmaceutical Co. A.S. (Ankara, Turkey). BPA (228 g mol⁻¹; C₁₅H₁₆O₂; CAS No: 80-05-7; purity: 99.9%) and ciprofloxacin (331 g mol⁻¹; C₁₇H₁₈FN₃O₃; CAS No: 85721-33-1; purity ≥98%) were purchased from Sigma-Aldrich (USA). Potassium persulfate (PS, K₂S₂O₈, >99.5%) was purchased from Sigma-Aldrich, (USA). HPLC-grade acetonitrile (ACN) and methanol (MeOH) were obtained from Merck (Germany). Aqueous MP solutions were prepared in distilled water (Arium 61316RO, Sartorius AG, Germany). The RSW sample was taken from the influent (TOC=7.6 mg/L; DOC=7.2 mg/L; SS=12 mg/L; color=48 Pt-Co units; alkalinity=115 mg CaCO₃/L; hardness=110 mg CaCO₃/L; phosphate= 0.17 mg/L; sulfate=15.5 mg/L; nitrate=2.2 mg/L; chloride=21 mg/L; pH=7.9.) of a local water treatment plant located in Istanbul, Turkey.

Experimental procedures
Aqueous MP solutions were treated in a 500 mL-capacity borosilicate glass reactor at room temperature (25±2 °C) at a fixed initial MP concentrations of 2 mg/L (BPA=8.8 µM; OPEO=4.7 µM; IOPA=2.6 µM; CIP=6.0 µM) based on the calculated detection limits for both HPLC and bioassays and enabled direct analytical assessment of individual samples without further concentration. 2 mg/L of MPs aqueous solutions were treated at pH 3 with 1 g/L ZVAl for 120 min in all experiments. The selection of the studied working conditions was based on preliminary experiments that have been reported recently (Arslan-Alaton et al., 2016a, b). The experimental procedure of a typical run was described elsewhere (Girit et al., 2015). Samples were taken at regular time intervals from the reactor and filtered through 0.22 µm Millipore membranes (Millipore Corp., USA) to separate ZVAl from the reaction solution. All experiments were conducted in duplicate and average values were taken when presenting the results.

Analytical procedures and instrumental analyses
An Agilent 1100 system (Agilent Technologies, USA) with a diode array detector (DAD) was employed for the measurement of MPs. The chromatographic conditions used for BPA, OPEO and IOPA have been described in elsewhere (Arslan-Alaton et al., 2016a, b; Girit et al., 2015). For CIP measurement, a C18 Novapack column (3.9mm×150mm; 5µm particle size; Waters, USA) was employed as a stationary phase, while the mobile phase was a mixture of 0.1% CH₃O₂/MeOH-H₂O (60:40, v/v). The flow rate and temperature of the column were set as 0.8 mLmin⁻¹ and 25°C, respectively. The instrument detection limits of OPEO, IOPA, CIP and BPA for an injection volume of 100 µL were calculated as 28µgL⁻¹, 78µgL⁻¹, 3.3µgL⁻¹ and 3.0µgL⁻¹, respectively.

Acute toxicity and genotoxic activity measurements
Before conducting the toxicity tests, residual oxidant in the test samples were removed with Sodium thiosulfate to eliminate the interference of PS in bioassays (Olmez-Hanci et al., 2014). In order to eliminate its interference with the toxicity and genotoxicity test results Al³⁺ residuals in the reaction solutions were removed in the form of Al(OH)₃ flocs by pH adjustment to 6-7, precipitation and membrane filtration steps prior to toxicity analysis.
Acute toxicity

The toxicity towards the photobacterium V. fischeri was measured with a BioTox™ test kit (Aboatox Oy, Finland) in accordance with the ISO 11348-3 (2008) protocol. The acute toxicity towards the freshwater microalgae P. subcapitata was determined using Algaltoxkit F™ (MicroBioTests, Inc., Gent, Belgium) micro-biotests according to the procedure described in ISO 8692 (2012). The application of these standard methods for the assessment of toxicity on V. fischeri and P. subcapitata was explained in more detail elsewhere (Olmez-Hanci et al., 2014). Acute toxicity results were reported as the percent relative inhibition with respect to a control during MPs treatment in DW and RSW samples. A positive control sample with potassium dichromate was also included for each test and all bioassays were run in triplicate.

Genotoxicity

The umuC assay was carried out according to the procedure described by ISO 13829 (2000). The UMU-Chromo Test™ test kit was supplied by EBPI Environmental Bio-Detection Products Inc. (Canada). In the present study, several dilutions (namely 1:1.5, 1:3.0, 1:6 and 1:12) of the original and treated MP samples together with positive, negative and solvent controls were tested in accordance with the test protocol. For each sample dilution, the growth factor G, the β-galactosidase activity US and induction ratio IR were calculated. The whole test was considered valid if the positive controls reach an IR >2. Calculation of G allowed to identify toxic growth inhibitory effects and G<0.5, representing >50% inhibition of the biomass growth, was considered to be indicative of samples being cytotoxic. An IR >1.5 was taken as the threshold at which the sample was considered as genotoxic (ISO 13829, 2000).

3. Results and Discussion

Treatability of MPs in distilled and raw surface water

In order to assess the oxidative capacity of the ZVAI/PS treatment system for MPs removal, degradation experiments were conducted under the following optimized reaction conditions: MPs=2mg/L; ZVAI=1g/L; pH=3; PS=0.25mM (for CIP and BPA) and 0.50mM (for OPEO and IOPA). Figure 1 (a) and (b) presents time dependent changes in OPEO, IOPA, CIP and BPA concentrations during ZVAI/PS treatment combination in DW and RSW, respectively. In addition to ZVAI/PS process, the degradation of MPs with mere PS oxidation (in the absence of ZVAI) and nZVAI/O2/H+ treatment (in the absence of PS) were also examined in DW. PS alone was not capable of degrading complex organics including the investigated MPs. On the other hand 22% OPEO, 8% IOPA, 58% CIP and 18% BPA removals were evident for nZVAI/O2/H+ treatment (data not shown). As expected, PS activation with ZVAI greatly enhanced the degradation rates of MPs. OPEO and CIP were completely degraded after 90 and 120 min treatment with ZVAI/PS in DW whereas 94% IOPA and 98% BPA removals were achieved after 120 min. Speaking for the results in actual water samples, a dramatic decrease in OPEO, IOPA, CIP and BPA removal rates was observed in RSW owing to the presence of organic and inorganic competitors for SO4••. The corresponding OPEO, IOPA, CIP and BPA removal efficiencies in RSW were 59%, 29%, 73% and 46%, respectively. These attained results are consistent with the presence of organic and inorganic matter in the RSW matrix capable of scavenging SO4•• as happens with humic acids, NO3 or Cl− in natural waters that inhibit the overall treatment performance.
Changes in acute toxicity and genotoxic activity

Considering that the degradation and toxicity pattern of MPs will be affected by the characteristics of the actual water sample, changes in acute and genotoxicity were examined during ZVAI/PS treatment of MPs in DW and RSW. In this section, percent relative inhibition values before \((t=0)\) and during ZVAI/PS treatment of MPs in RSW sample towards \(V.\ fischeri\) and \(P.\ subcapitata\) (Figure 2a and b, respectively) were presented due to space limitations. Toxicity analysis of original and ZVAI/PS-treated MP samples demonstrated different patterns for the studied test organisms. The percent relative inhibitions of the original (untreated) OPEO, IOPA, CIP and BPA towards \(V.\ fischeri\) were in order of CIP (42%)>IOPA (27%)>BPA (12%)>OPEO(6%). CIP appeared to be the most toxic MP towards \(V.\ fischeri\). As can be followed from Figure 2, the inhibitory effect of aqueous MP solutions towards \(V.\ fischeri\) fluctuated through the reaction, most probably due to the formation and subsequent oxidation of degradation products of MPs and eventually decreased to practically non-toxic levels for OPEO and BPA whereas 19% and 23% relative inhibition was still evidenced for OPEO and CIP, respectively. \(P.\ subcapitata\) toxicity patterns differed appreciably; during ZVAI/PS treatment of BPA, percent relative inhibition increased from 56% to 64% after 120 min which was not practically different from that of the untreated BPA. In case IOPA, the relative inhibition fluctuated during treatment and reached a value (85%) which was not practically different from that of the untreated IOPA (88%). On the other hand, OPEO degradation products exhibited a low toxic effect towards \(P.\ subcapitata\) after 120 min (around 25%). The increasing and decreasing trend of toxicity towards \(V.\ fischeri\) and \(P.\ subcapitata\) was also evidenced during ZVAI/PS treatment of the investigated MPs in DW. In general the bioassay performed with \(P.\ subcapitata\) in DW appeared to be more sensitive to the investigated MPs degradation products among the selected bioassays.

Figure 1. Changes in OPEO, IOPA, CIP and BPA concentrations during ZVAI/PS treatment system in DW (a) and RSW (b). MP=2 mg/L; DOC\(_{RSW}\)=7.2 mg/L; ZVAI=1 g/L; PS=0.25 mM for CIP and BPA; PS=0.50 mM for OPEO and IOPA; pH=3; T=25°C.

Figure 2. \(V.\ fischeri\) and \(P.\ subcapitata\) acute toxicity evolution based on percent relative inhibition rates observed during ZVAI/PS treatments in DW (a) and RSW (b). Treatment conditions: MP=2 mg/L; DOC\(_{RSW}\)=7.2 mg/L; ZVAI=1 g/L; PS=0.25 mM for CIP and BPA; PS=0.50 mM for OPEO and IOPA; pH=3; T=25°C.

Figure 3 presents the \(I_R\) values obtained for the untreated and ZVAI/PS-treated OPEO, IOPA, CIP and BPA in DW. The calculated G values demonstrated that neither the original nor the treated
products of OPEO, IOPA and BPA were cytotoxic. Only CIP was found to be cytotoxic at the studied dilution ratios and due to G < 0.5 the IR could not be calculated. Both untreated (Figure 3a) and ZVAI/PS-treated (Figure 3b) OPEO, IOPA and BPA samples had no genotoxic activity according to the umuC test results. However, the ZVAI/PS treatment of CIP in DW revealed the formation of genotoxic degradation products after 120 min of reaction time.

Figure 3. Evolution of genotoxic effects of the untreated (a) and nZVAI/PS treated (b) OPEO, IOPA, CIP and BPA samples in DW. Treatment conditions: MP=2 mg/L; DOC_{RSW}=7.2 mg/L; ZVAI=1 g/L; PS=0.25 mM for CIP and BPA; PS=0.50 mM for OPEO and IOPA; pH=3; T=25°C.

Conclusions and Recommendations
In the present study, activation of persulfate (PS) with nanoscale zero valent aluminum (nZVAI; 1 g/L) particles was investigated in distilled water (DW) and raw surface water (RSW) samples for the treatment of 2 mg/L Bisphenol A (BPA), octyphenol ethoxylate (OPEO), Iopamidol (IOPA) and ciprofloxacin (CIP) at pH 3 for 120 min. Changes in acute and genotoxicity patterns during ZVAI/PS treatment of selected micropollutants were particularly studied. The major findings of this work are summarized below:

- PS activation with nZVAI greatly enhanced the degradation rates of OPEO, IOPA, CIP and BPA.
- The decreasing order of MP removal efficiencies in DW are; OPEO>CIP>BPA>IOPA.
- The environmental characteristics of the water/wastewater matrix (its inorganic and organic matter content) represented a drawback for the MPs removal. The treatment efficiency of the nZVAI/PS system in RSW followed the decreasing order of CIP>OPEO>BPA>IOPA.
- Toxicity bioassays showed that the inhibitory effect of the MPs and their degradation products differed according to the water matrix and the test organisms.
- According to the UMU-Chromo test results, only CIP was found to be cytotoxic at 2 mg/L initial concentration and ZVAI/PS-treated CIP samples resulted in the formation of genotoxic degradation products.

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References


Zero-Valent Aluminum-Mediated Degradation of Bisphenol A in the Presence of Common Oxidants

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Keywords: Bisphenol A, zero-valent Aluminum, Oxidants, Acute Toxicity, Surface Water, Reuse.

Abstract

Bisphenol A (BPA) is an industrial pollutant being considered as one of the major endocrine disruptors found in natural water bodies. In the present study, the use of a commercial, nanoscale zero valent aluminum (ZVAl) powder was examined for the treatment of 2 mg/L, aqueous BPA solution. The study focused on i) hydrogen peroxide (HP) and persulfate (PS) activation with ZVAl to accelerate the oxidation reaction, ii) treatment performance in real freshwater samples, iii) effects on acute toxicity and iv) reuse potential of ZVAl nanoparticles after ZVAl/HP and ZVAl/PS treatments. In pure water, ZVAl coupled with HP or PS provided an effective treatment of BPA particularly when PS was employed as the oxidant. On the other hand, in BPA-spiked surface water the ZVAl/HP treatment combination outperformed ZVAl/PS oxidation in terms of BPA removal, whereas ZVAl/PS oxidation was superior on the basis of total/dissolved organic carbon (TOC/DOC) removals. According to the bioassays conducted with the marine photobacteria *Vibrio fischeri* and the freshwater microalgae *Pseudokirchneriella subcapitata*, the acute toxicity of BPA exhibited substantial fluctuations during ZVI/PS treatment in pure and real surface water samples.

1. Introduction

Endocrine Disrupting Compounds (EDCs) can mimic hormones, bioaccumulate in sewage sludge and soil sediments, may cause reproductive toxicity and cancer besides other harmful effects on human health and the ecological environment (Sharma et al., 2016). Among the potential EDCs, Bisphenol A (BPA) is one of the most well-known and studied EDC. It is an important raw material being widely used as a monomer for the production of polycarbonates, epoxy resins, plasticizers, flame retardants, dental sealants, thermal papers, printing ink, antioxidants, paints and other chemicals (Li et al., 2016). It leaches into the environment from utility items such as toys, baby feeding bottles, plastics and tiffin carriers. Considering its estrogenic and mutagenic/teratogenic effects, effective and ecotoxicologically safe means of eliminating BPA from the environment has become a priority task.

Recently, a number of treatment approaches, such as biodegradation with algae, fungal treatment, adsorption and advanced oxidation processes including sonolysis, catalytic ozonation, photochemical oxidation, photocatalysis and the Fenton’s reagent have been explored for the degradation of BPA (Li et al., 2016; Sharma et al., 2016). Among these treatment methods, zero-valent metals such as zero-valent iron (ZVI; \(E^0= -0.43\) eV) and zero-valent aluminum (ZVAl; \(E^0= -1.66\) eV) have received major attention recently due to their unique surface properties, high abundance and superior thermodynamic driving force
Both metals have already been explored for the treatment of heavy metals, pesticides, halogenated phenol derivatives, dyes, bromate, nitrate and perchlorate found in ground and surface water (Lin et al., 2016; Chen et al., 2015). Like the more well-known and studied ZVI, ZVAl may activate molecular oxygen to produce reactive oxygen species including hydrogen peroxide (HP), superoxide radical (O$_2^\bullet^-$) and hydroxyl radical (HO$^\bullet$). The ZVAl/H$^+$/O$_2$ treatment system involves two mechanisms; the corrosive dissolution of Al$^{3+}$ and simultaneous reduction of O$_2$ to hydroperoxyl radical (HO$_2^\bullet^-$) leading to the formation of HP and the generation of HO$^\bullet$ by an electron transfer mechanism from ZVAl to O$_2$ producing HP as given below (Chen et al., 2015):

$$\text{Al}^0 \rightarrow \text{Al}^{3+} + 3e^-$$  \hspace{1cm} (1)

$$\text{O}_2 + \text{H}^+ + e^- \rightarrow \text{HO}_2^\bullet$$  \hspace{1cm} (2)

$$2\text{HO}_2^\bullet \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$$  \hspace{1cm} (3)

$$\text{Al}^0 + 3\text{H}_2\text{O}_2 \rightarrow \text{Al}^{3+} + 3\text{HO}^\bullet + 3\text{OH}^-$$  \hspace{1cm} (4)

The degradation of micropolllutants by the ZVAl/H$^+$/O$_2$ treatment system is a relatively slow and inefficient process. Depending on the surface properties of ZVAl as well as the pH of the reaction solution, an induction period (lag phase) is typically being observed for the removal of pollutants by the ZVAl/H$^+$/O$_2$ treatment system. Therefore, external addition of common oxidants such as HP or persulfate (PS) is expected to enhance pollutant removal rates and efficiencies. Enhanced HO$^\bullet$ and sulfate radical (SO$_4^\bullet^-$) formation during ZVAl treatment in the presence of HP (eqn. 4) and PS, respectively, starts with an electron transfer from the ZVAl surface to the oxidants under acidic pH values (pH<4):

$$\text{ZVAl/PS/H}^+: \hspace{1cm} 2\text{Al}^0 + \text{S}_2\text{O}_8^{2-} + 6\text{H}^+ + 1.5\text{O}_2 \rightarrow 2\text{Al}^{3+} + 2\text{SO}_4^{\bullet^-} + 3\text{H}_2\text{O}$$  \hspace{1cm} (5)

Considering the great potential of ZVAl-mediated oxidation of micropolllutants and the serious gap in real-scale, advanced water treatment applications, the present study focused on the degradation of aqueous BPA, selected as the model EDC and micropolllutant, in pure water (PW) and real surface water (SW) samples. HP and PS were selected as the oxidizing agents and activated with nano-scale ZVAl powder to enhance BPA oxidation. Besides BPA and total/dissolved organic carbon (TOC/DOC) evolution, oxidant consumption, acute toxicity towards the marine photobacteria *Vibrio fischeri* (*V. fischeri*) and the freshwater microalgae *Pseudokirchneriella subcapitata* (*P. subcapitata*) as well as the ZVAl reuse potential were also examined within the scope of this experimental study.

2. Materials and Methods

**Materials**

High purity (> 99.5%) ZVAl nanoparticles, with an average particle size of 100 nm and a specific BET surface area of 10-20 m$^2$/g, were purchased from US Research Nanomaterials, Inc. (Houston, Texas). An initial BPA concentration of 2 mg/L was selected in this work due to several reasons. Firstly, 2 mg/L is an appropriate concentration to easily and accurately follow BPA abatement kinetics via instrumental analyses; secondly, it is a suitable working range that could easily be compared with previous related work and thirdly, it has been reported in the scientific literature that BPA concentrations in the “mg/L” range are the highest concentrations being encountered in natural/engineered systems (in landfill leachate, for example). Hence, 2 mg/L can be considered as a worst-case scenario in terms of BPA concentration. The raw SW sample was taken from the influent of a local water treatment plant.
located in Istanbul, Turkey. The main environmental characteristics of the SW sample were TOC=6.48 mg/L; DOC=6.23 mg/L; SS=12 mg/L; color=48 Pt-Co units; alkalinity=115 mg CaCO$_3$/L; hardness=110 mg CaCO$_3$/L; phosphate=0.17 mg/L; sulfate=15.5 mg/L; nitrate=2.2 mg/L; chloride=21 mg/L; pH=7.9. All other chemicals and reagents used in this study were of analytical grade and purchased either from Fluka, Merck (Germany) or Sigma-Aldrich Chemicals (USA).

**Experimental procedures**

Several control (ZVAI only, HP and PS only experiments) and treatability (optimization) experiments were carried out in 500 mL-capacity glass beakers under continuous stirring at 150 rpm to ensure uniform ZVAI dispersion, mixing and oxygen saturation. Firstly, aqueous BPA solution (2 mg/L, 8.8 $\mu$M) was prepared in PW and its pH was adjusted to 3 with concentrated $\text{H}_2\text{SO}_4$ solution. Thereafter, the desired amount of ZVAI nanopowder was added into the reaction solution. Finally, the oxidant (HP or PS) was introduced to initiate the oxidation reaction. All experimental working conditions (pH, ZVAI, HP and PS concentrations, treatment time) were selected considering former related studies (Cheng et al., 2015; Arslan-Alaton et al., 2016). BPA-spiked, real SW samples were subjected to ZVAI/HP and ZVAI/PS treatment under optimized reaction conditions.

**Analytical procedures and instrumental analyses**

All samples containing ZVAI were immediately filtered through 0.22 micron Millipore membranes (Millipore Corp., USA) to separate the ZVAI nanoparticles from the reaction solution. Thereafter, samples were directly analyzed for remaining BPA, DOC, HP and PS concentrations. The pH of the original and treated samples was adjusted to neutral (7.0±0.2) values with concentrated NaOH solution before conducting the bioasays. BPA analysis was performed on a HPLC (Agilent 1100 Series, Agilent Technologies, USA) equipped with a diode array detector (G1315A, Agilent Series) and a Symmetry C18 (3.9 mm×150 mm, Waters, USA) reversed phase column. The detection wavelength and column temperature were set as 214 nm and 25°C, respectively. The mobile phase consisted of acetonitrile/water (50/50, v/v) used at a flow rate of 1.0 mL/min. The quantification limit of BPA for an injection volume of 100 $\mu$L was calculated as 10 times of the signal-to-noise ratio (28.0 $\mu$g/L). The TOC/DOC content of the samples was measured on a $V_{\text{PCN}}$ analyzer (Shimadzu, Japan). Residual HP and PS concentrations were traced by employing colorimetric methods according to Klassen et al. (1994) and Villegas et al. (1963).

Acute toxicity bioassays

The acute toxicity experiments were conducted with original and ZVAI/PS-treated BPA in PW and SW. Toxicity towards the photobacterium $V. \text{fischeri}$ was measured using a commercial bioassay kit (BioToxTM, Aboatox Oy, Finland) according to the ISO 11348-3 test protocol (2008). Percent relative photoluminescence inhibition rates were calculated after 15 min incubation on the basis of a toxicant-free control. The acute toxicity towards the freshwater microalgae $P. \text{subcapitata}$ was examined using Algaltoxkit $F^\text{TM}$ (MicroBioTests, Inc., Belgium) microbiotests according to ISO 8692 (2012). At the start and after 24, 48 and 72 h, the cell density in the test replicates were measured on 10 cm path-length cuvettes at 670 nm, using a Jenway 6300 model spectrophotometer (Bibby Scientific, USA). Percent relative growth inhibition rates were calculated after 48 h incubation on the basis of a toxicant-free control. In order to eliminate their effect on acute toxicity measurements, residual PS was removed with
sodium thiosulfate (Merck, Germany), which was found to be the most suitable quenching agent to eliminate the interference of PS in the *V. fischeri* and *P. subcapitata* bioassays.

3. Results and Discussion

**Preliminary control and optimization experiments**

Control experiments have indicated that in the absence of either ZVAl (1 g/L) or oxidants (0.5 mM HP, PS) only poor and slow BPA degradations were obtained (pH=3, t=120 min). BPA removal was limited to <10% and <20% at the end of HP/PS oxidation and ZVAl/H⁺/O₂ treatment, respectively (data not shown). After some preliminary optimization experiments that were carried out at varying HP and PS concentrations (0-2.5 mM), ZVAl concentrations (1-5 g/L), pH’s (3-7) and for t=120 min, it was decided to work under the following, optimum reaction conditions; 0.25 mM PS-HP, 1 g/L ZVAl, pH=3, t=120 min. In the forthcoming experimental runs, only results being achieved under the above given, optimized reaction conditions together with the respective controls were presented due to space limitations.

**Treatability in pure and real surface water**

Figure 1 presents ZVAl-mediated BPA removal in PW and SW in the absence and presence of HP or PS oxidants. In PW, BPA removal increased from 18% to 72% and 100% after 120 min in the presence of HP and PS, respectively, as a consequence of accelerated HO• and SO₄•⁻ production, respectively. In the SW medium, BPA removals increased from these values up to 94% BPA removal for ZVAl/HP treatment, whereas a dramatic inhibition to 46% BPA removal was evident for the ZVAl/PS combination, accompanied with 9% (ZVAl/HP) and 22% (ZVAl/PS) DOC removals at the end of treatment. Apparently, BPA degradation and mineralization (DOC abatement) rates were influenced by the type of oxidant producing different reactive oxygen species as well as the treatment medium (i.e. the presence of organic/inorganic components in the SW sample). In previous experimental work carried out with free radical probe chemicals (alcohols), it could be established that HO•(ZVAl/HP) and SO₄•⁻(ZVAl/PS)-driven AOPs exhibited different reactivities and selectivities for different model pollutants and their degradation products. In the present study it was evident that in SW (i.e., the presence of DOC) BPA removal was hindered during ZVAl/PS treatment; however, BPA removal was not affected by ZVAl/HP treatment. DOC removal was retarded when BPA was subjected to ZVAl/HP treatment, resulting in only 9% DOC removal in SW. On the other hand, 22% DOC removal was obtained after 120 min ZVAl/PS oxidation of BPA in SW, indicating that DOC abatement was not inhibited during ZVAl/PS treatment.

**Ecotoxicological assessment**

Acute toxicity studies were conducted for ZVAl/PS treatment in PW and SW samples. ZVAl/PS treatment was selected for ecotoxicological assessment since no appreciable mineralization (TOC/DOC removals) was achieved with the ZVAl/HP treatment system. Figure 2 depicts changes in percent relative inhibition values during BPA treatment with the ZVAl/PS system. BPA toxicity appeared to be substantially higher for *P. subcapitata* (in the range of 38-85%) than for *V. fischeri* (in the range of 10-20%) and fluctuated throughout ZVAl/PS treatment. As is apparent from Figure 2, acute toxicity patterns also depended upon the water matrix; at least two-fold higher inhibition rates were obtained in SW than in PW revealing that SW ingredients negatively affected acute toxicity results. Moreover, *P. subcapitata* was more sensitive towards BPA and its oxidation products than *V. fischeri*. It should be mentioned here that in both cases the acute toxicity was not attributable to Al residuals, because Al ions were
successfully removed in the form of \( \text{Al(OH)}_3 \) flocs after a pH-re-adjustment, precipitation and filtration step. It was also not due to the presence/accumulation of sulfate or other sulfur forms during ZVAl/PS experiments, as was already confirmed in previous work (Arslan-Alaton et al., 2016).

**Reuse potential**

ZVAl was re-used in five consecutive cycles for BPA removal in PW after thoroughly rinsing with deionized water, 0.22 micro-filtration and drying at 110 °C for 4-5 h. Figure 3 displays percent BPA removal efficiencies obtained after each reuse cycle. It could be demonstrated that BPA removals remained in the range of 90-100% after ZVAl/PS treatment for five consecutive cycles in the presence of HP, whereas in the case of ZVAl/PS treatment, BPA removal dropped from 100% to around 60% beyond the 4th reuse cycle.

**Figure 1.** Changes in BPA concentrations during ZVAl, ZVAl/HP, ZVAl/PS treatments in PW and SW samples. Experimental conditions: BPA\(_0\)=2 mg/L; HP\(_0\)=PS\(_0\)=0.25 mM; ZVAl=1g/L; pH\(_0\)=3.0; t=120 min; DOC\(_0\) of SW=6.2 mg/L.

**Figure 2.** 15 min-\( V. \text{fischeri} \) and 48 h-\( P. \text{subcapitata} \) acute toxicity evolution based on percent relative inhibition rates observed during ZVAl/PS treatments in PW and SW. Experimental conditions: BPA\(_0\)=2 mg/L; HP\(_0\)=PS\(_0\)=0.25 mM; ZVAl=1g/L; pH\(_0\)=3.0; t=120 min; DOC\(_0\) of SW=6.2 mg/L.

**Conclusions and Recommendations**

Treatability of BPA with ZVAl-activated HP and PS in PW and SW samples was investigated. Oxidation (BPA, TOC/DOC) performance, ecotoxicological assessment and ZVAl reuse potential in the presence of HP and PS demonstrated that both proposed treatment systems (ZVAl/HP and ZVAl/PS) have a promising application potential for efficient BPA degradation and mineralization.
However, further challenges exist and are suggested for future studies;

- The reaction mechanism of treatment systems using ZVAI are very complex and have not been fully explored yet. Hence, more detailed assessment is required in this relatively untouched research field.
- Until now, most studies were carried out in lab-scale. These results may not reflect the actual treatment performance in real water and wastewater.
- Treatability in real water and wastewater matrices are encouraged to question the practical utility of ZVAI for water and wastewater treatment.

Figure 3. Percent BPA removal efficiencies obtained after ZVAI/PS treatment in PW with ZVAI reused for five cycles. Experimental conditions: BPA_{0}=2 mg/L; HP_{0}=PS_{0}=0.25 mM; ZVAI=1 g/L; pH_{0}=3.0; t=120 min.

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References
The Role of Energy Consumption in Optimized Operation of Electrochemical Advanced Oxidation Processes: Fered-Fenton Reactor

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Keywords: Sustainable water management, reuse, Fered-Fenton energy consumption, advanced oxidation technology, waste reduction, artificial neural network

Abstract

High energy consumption has been reported as a hindrance to efficient implementation of electrochemical processes which have been introduced as an environmentally friendly method in water reuse issues along sustainable water management. In this paper while maintaining system efficiency in an acceptable level, electrical energy consumption in the previously introduced electrochemical advanced oxidation reactor of Fered-Fenton is optimized for sludge stabilization by investigation of affecting parameters including inflow organic concentrations, retention time, inter-electrode distance, sodium sulfate concentrations and the ratio of electrodes surface area to reactor volume. Regarding the performed experiments and analyses, it's declared that utilizing graphite electrodes with inter-electrode distance of 12.5-15 mm, 0.056-0.111 mol/L sodium sulfate concentrations and electrodes surface area of 100 cm²/L leads to an acceptable level of ≥80 system efficiency and electrical energy consumption of 0.8-1.6 kWh/(kg VSS removal) after 90-210 minutes of the experiment. It shows considerable efficiency and less energy consumption of Fered-Fenton process for waste-activated sludge stabilization compared with conventional methods accordingly. It was also determined that the higher the concentrations of inflow organics is, the more cost effective the system would be. In order to find a correlation between the parameters and to predict the system function in different scenarios, KSOFM and MLP neural networks were successfully utilized.

1. Introduction

Sustainable water management can be defined as water resource management that meets the needs of present and future generations. Water reuse is integral to sustainable water management because it allows water to remain in the environment and be preserved for future uses while meeting the water requirements of the present (U.S.EPA, 2012). Electrochemical advanced oxidation processes (AOPs) in wastewater treatment have been receiving more attention in recent years, due to its distinctive advantages such as environmental compatibility, versatility, safety, selectivity, amenability to automation, fast treatment rate, convenience and simplicity (Brillas and Casado, 2002; Chen, 2004; Rajeshwar et al., 1994). It may be considered as an 'economical alternative process' for the cases when conventional treatment methods fail to reduce pollution (Brillas et al., 1998). However, high energy consumption of electrochemical treatment and related high running costs of the process confines larger scales application of these methods (Chen, 2004; Gholikandi, 2015(a); Szpyrkowicz et al., 2005).

In previous investigations (Gholikandi, 2015(b); Gholikandi et al., 2014) research group introduced electrochemical advanced oxidation reactor of Fered-Fenton as a novel method of
This method was proved to be efficient with higher degradation rate of organics than traditional ones. Reactions (1) and (2) are the most important and effective reactions occurring in this system so that hydroxyl radical which is the main oxidation factor of organics be produced (Brillas et al., 2009; Fytiti and Zabaniotou, 2008; Gholikandi et al., 2014).

\[
\begin{align*}
Fe^{2+} + H_2O_2 & \rightarrow Fe^{3+} + OH^- + OH^* \\
Fe^{3+} + e^- & \rightarrow Fe^{2+}
\end{align*}
\]

(1) (2)

Since high energy consumption has been reported as a hindrance to efficient implementation of electrochemical processes (Avsar et al., 2007; Güven et al., 2012), the aim of this work is to optimize energy consumption in Fered-Fenton process by determining the optimum range of operative parameters including inflow organic concentrations ([VSSin]), retention time (t), inter-electrode distance (D), sodium sulfate concentrations ([Na\textsubscript{2}SO\textsubscript{4}]) and the ratio of electrodes surface area to reactor volume (A/V) (Daneshvar et al., 2007; Fockey and Van Lierde, 2002; Martinez-Villafane and Montero-Ocampo, 2010; Modirshahla et al., 2008) in which VSS removal efficiency maintains an acceptable level of \( \geq 80\% \) and to compare its efficiency and energy consumption with traditional sludge stabilization methods.

### 2. Material and Methods

Pilot studies were conducted in 2014. Excess sludge samples were provided from return activated sludge site of Shahid Mahallati wastewater treatment plant in Tehran. Pilot reactor was a plexi glass cylinder of 0.9 liter, embedding two anodes and two cathodes of graphite. Electrodes dimensions, setting depth in sludge and contact surface of each electrode with sludge are 140×60×1, 100 and 100×60 mm, respectively. Stirring in reactor was done by using an electrical engine (Zheng, zs–ri, 6(V) DC, 366 rpm). Using magnetic stirrer was relinquished because of its negative effect on ferrous ion (Fe\textsuperscript{2+}) and its catalytic function in Fenton process. To adjust reactor amperage, digital power supply (Mps, DC–3003D, 0-3 (A), 0-30 (V)) was used. Chemicals including ferrous sulfate (FeSO\textsubscript{4}) and hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) (Fenton's reagent), sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) and sodium hydroxide (NaOH) (to adjust pH), sodium sulfate (Na\textsubscript{2}SO\textsubscript{4}) (to generate electrical conductivity), and filter papers (No. 42) were provided from Merck and Whatman company, respectively. Laboratory pilot is explained in detail in 0.

Primarily, sludge pH was adjusted by sulfuric acid and sodium hydroxide and then an initial sample of 50 cc was taken to measure initial VSS. Next, ferrous sulfate and hydrogen peroxide were injected to the reactor. Electrodes were set in the reactor after connecting to the power supply and ampere was then adjusted on 0.65 mA. After 240 minutes, a secondary sample was taken from reactor depth of 80 mm and voltage was measured during the experiment. All the experiments were conducted according to standard methods (APHA, 2012) and each set of experiments were repeated three times to control errors. Electrical energy consumption for removal of 1 kg VSS (UED) is calculated by using equation (3) (Ghosh et al., 2011).

\[
UED \left( \frac{kwh}{kg VSS \text{ removal}} \right) = \frac{V \times I \times t}{\left[\frac{\text{VSS in} \times \eta}{1000} \right]} \times \frac{v}{\nu}
\]

Where UED is unit energy demand in kWh/kg VSS removal, V is voltage in volt, I is current intensity in Ampere, t is retention time in hour, v is reactor volume in liter, [VSSin] is concentrations of suspended solids in mg/L and \( \eta \) is VSS removal efficiency in percent.
obtained in previous researches, working conditions of the laboratory pilot are considered optimum (Gholikandi, 2015(b); Gholikandi et al., 2014).

3. Results and Discussion

Solution resistance cause potential drop which plays an effective role in cell voltage (Daneshvar et al., 2007). The higher the [VSSin] is, the more the system resistance would be. As a result potential drop increases and consequently the voltage of power supply increases to supply constant current intensity (650 mA). However UED decreases (Figure 2(a)) because it depends upon [VSSin] and VSS removal efficiency as well as voltage (equation (3)), and VSS removal efficiency increases as [VSSin] increases (Figure 2(a)). Therefore the higher the concentrations of inflow organics is, the less UED is consumed.

As time passes, system resistance decreases due to the reduction of organics concentrations; therefore potential drop and subsequently the voltage of power supply decreases. Since UED depends upon time as well as voltage, it increases as time passes (0Figure 2(b)). As it's shown in Figure 2(b), after 210 minutes of the beginning of the experiment, VSS removal efficiency reaches its maximum level and then becomes stable. This figure also illustrates that UED is directly related to retention time. Therefore regarding the acceptable level of VSS removal efficiency (≥80), optimum UED is achieved in the range of 90-210 minutes after the experiment.

When the distance between electrodes is increased produced ions move more slowly and system resistance increases which leads to potential drop increase; hence voltage of power supply increases. Therefore, as shown in Figure 2(c), UED increases. Concerning the acceptable level of VSS removal efficiency and the fact that inter-electrode distance is directly and linearly related to UED (Figure 2(c)) inter-electrode distance range to attain optimum UED is 12.5-15 mm.

As [Na2SO4] increases, electrical conductivity of the solution increases, movement rate of produced ions accelerates and system resistance decreases which leads to potential drop decrease. Consequently voltage of power supply decreases and according to equation (3) UED decreases (0Figure 2(d)). As it's observed in Figure 2(d), initial addition of sodium sulfate which generates electrical conductivity, decreases a great deal of UED (UED decreases 1.43 kWh/(kg VSS removal) for 0.056 mol/L increase in [Na2SO4]). Increasing sodium sulfate concentrations decreases UED demand too; however, very much more gently (UED decreases 0.31 kWh/(kg VSS removal) for 0.277 mol/L increase in [Na2SO4]) because of the existence of electrical conductivity which already had been generated. Due to the mentioned trend of UED and the acceptable level of VSS removal efficiency (Figure 2(d)), the range of [Na2SO4] to achieve optimum UED is 0.056-0.111 mol/L.

Increasing electrodes surface area causes system resistance to decrease and current intensity (I) to increase (in all experiments current density was considered constant, equal to 2.7 mA/cm² electrode.L). Therefore according to equation (4), voltage is constant and UED increases due to the increase in current intensity (Figure 2(e)).

\[ V = R \times I \] (4)

As it's illustrated in Figure 2(e), VSS removal efficiency is directly related to A/V up to 200 cm²/L (VSS removal efficiency does not change by A/V more than 200 cm²/L). On the other
hand, it is declared that UED is directly and linearly related to A/V. Since at electrodes surface area of 100 and 200 cm$^2$/L, there is no prominent difference in system efficiency however there are large difference of UED (Figure 2(e)) and electrodes surface area, it's logical to ignore two percent rise in efficiency to lessen the consumption of electrical energy and electrodes surface area and consequently lower costs. Therefore the electrodes surface area of 100 cm$^2$/L is adopted for reactor operation.

In order to find a correlation between the parameters and to predict the system function in different scenarios, Kohonen self-organizing feature maps (KSOFM) and Multilayer perceptron (MLP) neural networks were successfully utilized. Figure 3(a) shows correlations of process variables which are clustered using KSOFM neural network and the output maps presented by component plane visualization. The ranges of experimental data and KSOFM results are presented in Table 1. As can be seen, the KSOFM outputs correspond closely to experimental results. Therefore, the accuracy of experimental data was verified through KSOFM model.

The network structure that showed the best results in predicting VSS removal efficiency by utilizing MLP was composed of three layers: one input layer with five neurons consisting of t, D, [Na$_2$SO$_4$], A/V, UED; one hidden layer with 8 neurons; and one output with a single neuron (VSS removal efficiency). Since 8 neurons in the hidden layer show the highest R and the lowest MSE, it is selected as the hidden neuron numbers in this model. Regression analysis between the experimental and predicted values of the best network shows the R-value of about 1 for all data used for training, validation and testing which means there is high correlation between targets and outputs, that is, the ANN accurately predicted the VSS removal efficiency. This finding can be confirmed by Figure 3(b) in which the output is equal to experimental data.

Aerobic digestion is one of the basic traditional stabilization processes in current practice (Wang et al., 2008) in which VSS removal efficiency and UED are 35-50 percent and 2-3 kWh/(kg VSS removal) (Ghazy et al., 2011; Metcalf, 2003). This study demonstrates that Fered-Fenton process is approximately twice as efficient as sludge aerobic digestion (>80%) while consumes much less electrical energy (0.8-1.6 kWh/(kg VSS removal) with regard to consumed electrical energy in the system mixer).

### Table 1. The optimum range of experimental data and KSOFM results

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Experimental</th>
<th>KSOFM</th>
</tr>
</thead>
<tbody>
<tr>
<td>t (min)</td>
<td>90-210</td>
<td>190-210</td>
</tr>
<tr>
<td>D (mm)</td>
<td>12.5-15</td>
<td>14-15</td>
</tr>
<tr>
<td><a href="mol/L">Na$_2$SO$_4$</a></td>
<td>0.056-0.111</td>
<td>0.09-0.113</td>
</tr>
<tr>
<td>A/V (cm$^2$/L)</td>
<td>100</td>
<td>90.2-105</td>
</tr>
<tr>
<td>VSS removal efficiency</td>
<td>&gt;80%</td>
<td>80%</td>
</tr>
<tr>
<td>UED (kWh/kg VSS removal)</td>
<td>0.6-1.39</td>
<td>0.94-1.2</td>
</tr>
</tbody>
</table>

![Figure 1](image1.png)

**Figure 1.** Schematic of the laboratory Fered-Fenton reactor (1- Fered-Fenton reactor, 2- electrodes (anode and cathode), 3- electrical stirrer, 4- D.C. power supply, 5- variable D.C. power supply)
Figure 2. The relation of VSS removal efficiency and unit energy demand with (a) inflow VSS concentrations (t: 240 min, D: 15 mm, [Na₂SO₄]: 0.111 mol/L, A/V: 200 cm²/L) (b) retention time (D: 15 mm, [Na₂SO₄]: 0.111 mol/L, A/V: 200 cm²/L) (c) inter-electrode distance (t: 210 min, [Na₂SO₄]: 0.111 mol/L, A/V: 200 cm²/L) (d) sodium sulfate concentrations (t: 210 min, D: 15 mm, A/V: 200 cm²/L) (e) the ratio of electrodes surface area to reactor volume (t: 210 min, D: 15 mm, [Na₂SO₄]: 0.111 mol/L).

Figure 3. (a) KSOFM Visualization (b) MLP correspondence of Experimental data with network outputs
References


Green Synthesis of Clay/Silver Nanocomposite Materials for Adsorption of Hazardous Dyestuffs

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Keywords: Acacia cyanophylla, adsorbent characterization, dyestuff adsorption, green synthesis, leaf extract, nanocomposite

Abstract

In this study, clay/silver nanocomposite material (clay/AgNCs) was biosynthesized using Acacia cyanophylla extract, and the synthesized clay/AgNCs material was used as an adsorbent for adsorption of the Methylene Blue (MB) and Telon Blue AGLF (TB) dyes, known as hazardous dyestuffs. The optimum initial pH, temperature, and adsorbent concentration were determined to be 8.0, 45 °C, and 1.0 g L\textsuperscript{-1} for MB adsorption and 8.0, 55 °C, and 1.0 g L\textsuperscript{-1} for TB adsorption, respectively. The experimental equilibrium data for MB and TB adsorption were fitted well to the Freundlich and Langmuir isotherm models, respectively. Weber-Morris model results showed that both intraparticle and film diffusion were effective on the studied adsorption systems. The thermodynamic parameters showed that MB and TB adsorption on clay/AgNCs were endothermic, increasing in randomness of adsorbed species and spontaneous for MB adsorption, induced for TB adsorption. Moreover, clay/AgNCs were characterized by DLS, FT-IR, XRD, SEM and EDX analysis methods.

1. Introduction

Many investigations have been conducted on physico-chemical methods of removing colorful effluents, which include the use of coagulants, oxidizing agents, ultra-filtration, electro-chemistry, and adsorption. Most of these methods have limitations such as high capital and operational cost, low efficiency, sensitive operating conditions and production of secondary sludge. Adsorption by an eco-friendly adsorbent attracts attention as an economic and efficient method for water and wastewater treatment, especially dyestuff removal.

In recent years, there is a growing interest in the usage of metal nanoparticles (MeNPs) as adsorbents for dyestuff removal because they have significant advantages such as only a little amount of nanomaterial is required for removing of the pollutants from aqueous solutions, their adsorption capacities are relatively high because of high specific surface area and also a large number of unsaturated atoms on their surfaces (Thirumurugan et al., 2016).

There are various methods for the synthesis of MeNPs, such as complex synthesis/reduction procedures, co-precipitation, microemulsion, sonochemical, and photochemical techniques, but most of them are environmentally unfriendly and expensive. MeNPs are frequently prepared by chemical methods involving reducing agents, hydrazine hydrate, sodium boro-hydride, ethylene glycol, etc., which are very much hazardous to the environment. Thus, synthesis of MeNPs by living organisms such as bacteria, algae, fungi, and plants are currently paid more
attention. The using plant extract is more suitable due to its simplicity, cost efficiency, eco-
friendliness, and production of more stable nanoparticles in comparison with the using
microorganisms (Namvar et al., 2016). Also, the preparation of natural material/metal
nanocomposite materials has lately attracted much attention due to their cost efficiency, unique
structure, and properties. In this regard, some of MeNPs have also been synthesized in natural
materials, which have two-dimensional interlayer space, intercalation, swelling, and ion
exchange properties. Its interlayer space is used for the synthesis of MeNPs, as support for
anchoring transition-metal complex catalysts, and as adsorbents for various ions (Yunus et al.,
2009). In this respect; clay/silver nanocomposite material (clay/AgNCs) were biosynthesized
using Acacia cyanophylla extract, and used as adsorbent for adsorption of the methylene blue
(MB) and Telon Blue AGLF (TB) from aqueous solutions in this work.

2. Material Methods

2.1 Biosynthesis of Clay/AgNCs Nanocomposite Material

Fresh leaves of Acacia cyanophylla were washed with distilled water to purify of impurities
and then dried in an oven at 110 °C. A. cyanophylla leaf extract (LEx) was prepared by boiling
5.0 g of the dried leaves in 100 mL of distilled water at 100 °C for 120 min. The extract was
centrifuged to remove insoluble fractions and macromolecules. Lastly, the obtained dark yellow
extract was stored in the refrigerator for further the synthesis experiments. For clay/AgNCs
synthesis; 100 mL of 10^{-3} M AgNO_3 was firstly mixed
with 0.02 g of clay, and then 5.0 mL of
LEx at room temperature as natural reductant was dropped by syringe pump to the prepared
AgNO_3-clay mixture. The formation of clay/AgNCs was confirmed when the color of the
solution started to convert from transparent color to dark brown. The filtrate was washed
comprehensively with distilled water and then was dried at 110 °C in an oven for 24 h. The
clay/AgNCs were ground homogeneously by mortar and were stored in closed vessels in a
refrigerator for the adsorption experiments (Ahmad et al., 2011). Synthesized clay/AgNCs were
characterized by DLS, FT-IR, XRD, SEM and EDX analysis methods.

2.2 Adsorption Experiments

The adsorption experiments of TB and MB on clay/AgNCs were done in a batch system. 0.1 g
of clay/AgNCs, except for adsorbent concentration experiments, was mixed with 100 mL of the
desired initial dye concentration and initial pH in Erlenmeyer flasks. The flasks were agitated
on a shaker at constant temperature for 180 min to obtain adsorption equilibrium. Samples were
taken before mixing the adsorbent and dyestuff-bearing solution, then at predetermined time
intervals (in the range of 0.5–180 min) for the residual dyestuff concentration in the solution.
The unadsorbed TB and MB concentrations in supernatant were analyzed at 610 nm and 662
nm, respectively, with UV–vis spectrophotometer. Experiments were repeated for different
initial pH, initial dye concentration, temperature and adsorbent concentration values.

3. Results and Discussion

3.1 Characterizations of Clay/AgNCs

The diameter of single clay/AgNCs and the mean size with DLS analysis were determined as
160 nm (90 %) and 170 nm, respectively.

86
FT-IR spectrums of clay/AgNCs before and after adsorption were presented in Figure 1. Accordingly, the bands at 1622, 1373, and 1031 cm\(^{-1}\) corresponded to characteristic of amino acids containing NH\(_2\) groups (amide I band), C-N stretching vibrations of aromatic amine, and characteristic of C-OH stretching of secondary alcohols, respectively. These data showed the presence of amides, amine groups, and amino acid residues present in LEx in clay/AgNCs synthesis. The characteristic peaks of aromatic phenols at 800–600 cm\(^{-1}\) region (for C-H out of plane bend) were also observed in Figure 1 (Jagtap et al., 2013). Moreover, the characteristic bands of clay content were determined at 1031 cm\(^{-1}\) for Si-O in-plane stretching, 920 cm\(^{-1}\) for Al-OH-Al bending, and 796 cm\(^{-1}\) for Al-O stretching (Naowanat et al., 2016).

XRD patterns of clay/AgNCs before and after adsorption were shown in Figure 2. XRD pattern of the clay/AgNCs exhibited peaks at 2\(\theta\) angles of 38.10\(^{\circ}\), 44.28\(^{\circ}\), 64.50\(^{\circ}\), and 77.42\(^{\circ}\) which correspond to the [1 1 1], [2 0 0], [2 2 0], and [3 1 1] crystal planes of a cubic lattice structure of clay/AgNCs, respectively (Ghaedi et al., 2012). XRD pattern also revealed the presence of quartz, aluminosilicate, and feldspar phases related to clay (Noyan et al., 2007). Furthermore, it was observed that FTIR spectrums and XRD patterns of the clay/AgNCs before and after adsorption did not exhibit any differences, which was indicating physical adsorption processes.

![Figure 1. FT-IR spectrums of clay/AgNCs before and after adsorption](image)

![Figure 2. XRD patterns of clay/AgNCs before and after adsorption](image)

SEM images of clay/AgNCs with EDX spectrums before and after adsorption were presented in Figure 3. Accordingly, the porous structures were observed pre-adsorption, and these pores were covered by dyestuff molecules post-adsorption.

According to EDX analysis; the clay/AgNCs material before adsorption involved 32.4% O, 22.9% Ag, 19.6% Si, 18.3% C, 4.9% Al, 1.4% Fe, and 0.5% Mg. These results revealed the strong signal in the silver region and confirmed the formation of silver nanoparticles (AgNPs), and the determination of Si, Al, Mg peaks in EDX spectrum pre-adsorption indicated the
presence of clay. The spectral signals for carbon, oxygen, and nitrogen also indicated that the extracellular organic moieties from A. cyanophylla extract were also adsorbed on the surface of clay/AgNCs.

3.2 Effects of Environmental Conditions on the Adsorption

The effect of environmental conditions such as initial pH, initial dye concentration, adsorbent concentration and temperature on adsorption of TB and MB dyestuffs by clay/AgNCs was shown in Figure 4(a-d). From Fig. 4-a, it was observed that optimum initial pH values were found as 8.0 for MB and TB adsorption. In order to discuss the effect of initial pH; the zeta potential values of clay/AgNCs measured at different pH values (figure not shown) and the results showed that the adsorbent surface was negatively charged at the initial pH range of 2.5-13.5. Accordingly, the maximum adsorption capacities of clay/AgNCs were observed at the maximum zeta potential value (−24.93 mV) of the adsorbent surface because maximum electrostatic attraction occurred between negatively charged adsorbent surface and cationic structure dyestuff. From Figure 4-b, it was concluded that the equilibrium uptakes increased with increasing the initial TB concentration up to 300 mg/L and then slightly began to remain constant with further increase of initial TB concentration; on the other hand, the adsorption capacities increased linearly (qₑ=0.9691*Cₒ, R²=0.9997) with increasing initial MB concentration in the studied dyestuff concentration ranges as a result of the increase in driving force (∆C), which was giving the opportunity to work in the wide dyestuff concentration ranges. As can be seen from Figure 4-c, the adsorption percentage increased up to 1.0 g/L of adsorbent concentration, and then slightly decreased with further increase in adsorbent concentration while the equilibrium uptakes decreased with increasing the adsorbent concentration. The aggregation of clay/AgNCs at high adsorbent concentrations may result in a decrease in the active surface area and an increase in the diffusional path length, and so the lower adsorption capacities were observed at high adsorbent concentrations. As a result, the optimum adsorbent concentration for MB and TB adsorption was determined as 1.0 g/L. The effect of temperature was shown in Figure 4-d, the optimum temperature values for TB and MB adsorption were determined as 55 °C and 45 °C, respectively. Based on the results, the high adsorption capacities at high temperatures may be explained with the endothermic nature of the studied adsorption processes. This case was confirmed with thermodynamic parameters such as Gibb’s free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) calculating by Van’t Hoff equation (Table 1). From Table 1, the studied adsorption systems were endothermic (ΔH>0), increasing in randomness of adsorbed species (ΔS>0), and induced (ΔG<0) for MB adsorption, spontaneous (ΔG<0) for TB adsorption.
Table 1. Thermodynamic parameters

<table>
<thead>
<tr>
<th>Dyestuff</th>
<th>T (K)</th>
<th>ΔH (J/mole)</th>
<th>ΔS (J/mole.K)</th>
<th>ΔG (J/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Telon Blue AGLF</td>
<td>298</td>
<td>65651.5</td>
<td>200.0</td>
<td>5983.5</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td></td>
<td></td>
<td>4252.2</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td></td>
<td></td>
<td>1762.1</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td></td>
<td></td>
<td>149.4</td>
</tr>
<tr>
<td>Methylene Blue</td>
<td>298</td>
<td>23054.7</td>
<td>91.9</td>
<td>-4399.6</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td></td>
<td></td>
<td>-5169.6</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td></td>
<td></td>
<td>-6245.6</td>
</tr>
</tbody>
</table>

Figure 4. Effects of environmental conditions on the adsorption of TB and MB onto clay/AgNCs

3.3 Equilibrium, Kinetic, and Mass Transfer Modelling

Equilibrium modelling: The well-known Langmuir and Freundlich isotherm models were applied to the experimental equilibrium data at different temperatures and the isotherm constants from the linearized isotherm equations and regression coefficients were summarized in Table 2. According to Table 2, MB adsorption equilibrium was described with the Freundlich isotherm model while the TB adsorption equilibrium was defined with the Langmuir isotherm model. Also, as it was expected that the maximum adsorption capacities were obtained at optimum temperature values. The increase of the adsorption capacities of clay/AgNCs with increasing temperature may be explained with the endothermic nature of the studied adsorption processes.
Table 2. The isotherm model constants with regression coefficient values (R²)

<table>
<thead>
<tr>
<th>Dye</th>
<th>T (°C)</th>
<th>Langmuir isotherm model [q_e = Q_o b C_e / (1 + b C_e)]</th>
<th>Freundlich isotherm model [q_e = K_F C_e^{1/n}]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Qo</td>
<td>b</td>
</tr>
<tr>
<td>TB</td>
<td>25</td>
<td>78.64</td>
<td>0.00782</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>82.50</td>
<td>0.01197</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>716.33</td>
<td>0.00082</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>1209.19</td>
<td>0.00108</td>
</tr>
<tr>
<td>MB</td>
<td>25</td>
<td>50.62</td>
<td>0.03013</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>53.19</td>
<td>0.04003</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>60.97</td>
<td>0.07018</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>45.66</td>
<td>0.05883</td>
</tr>
</tbody>
</table>

3.3.1 Kinetic modelling

The adsorption kinetics of MB and TB onto clay/AgNCs were investigated by Lagergen’s pseudo first order \[\log(q_e - q_t) = \log(q_e) - k_1 t / 2.303\] and pseudo second order kinetic \[(t / q_t) = (1/q_e^2) k_2 + (t / q_e)\] models and the parameters of kinetic model and regression coefficients were given in Table 3. From Table 3, higher values of R² and the consistency between experimental and calculated uptake values showed excellent fit of the pseudo second order kinetics.

Table 3. Kinetics and mass transfer model parameters with R² values

<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>qEexp</th>
<th>Pseudo first order</th>
<th>Pseudo second order</th>
<th>Weber-Morris Model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>k₁</td>
<td>qₑcal₁</td>
<td>R²</td>
</tr>
<tr>
<td>TB</td>
<td>55.5</td>
<td>32.2</td>
<td>0.02579</td>
<td>22.3</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>100.0</td>
<td>56.7</td>
<td>0.02809</td>
<td>27.3</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>192.8</td>
<td>96.1</td>
<td>0.02855</td>
<td>35.6</td>
<td>0.86</td>
</tr>
<tr>
<td></td>
<td>277.8</td>
<td>181.7</td>
<td>0.03846</td>
<td>56.9</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>426.1</td>
<td>226.1</td>
<td>0.04260</td>
<td>53.1</td>
<td>0.66</td>
</tr>
<tr>
<td>MB</td>
<td>50.3</td>
<td>43.1</td>
<td>0.0177</td>
<td>12.9</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td>108.6</td>
<td>101.4</td>
<td>0.0263</td>
<td>26.3</td>
<td>0.79</td>
</tr>
<tr>
<td></td>
<td>208.6</td>
<td>199.9</td>
<td>0.0291</td>
<td>59.6</td>
<td>0.79</td>
</tr>
<tr>
<td></td>
<td>338.8</td>
<td>328.1</td>
<td>0.0403</td>
<td>115.5</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>520.1</td>
<td>506.4</td>
<td>0.0177</td>
<td>237.1</td>
<td>0.92</td>
</tr>
</tbody>
</table>

3.3.2 Effect of mass transfer: To evaluate the diffusion mechanism between dyestuff and clay/AgNCs, an intraparticle diffusion model proposed by Weber-Morris \(q_t = K_i t^{0.5} + I\) was used and the calculated parameters were presented in Table 3. If Weber–Morris plot of \(q_t\) versus \(t^{0.5}\) gives a straight line and pass through the origin, this means that only intraparticle diffusion controlled the adsorption process. On the other side, the Weber-Morris plot can be linear and
also has intercept value if the adsorption system follows both intraparticle and film diffusion. As understood from Table 3, both intraparticle and film diffusion were effective on MB and TB adsorption processes.

**Nomenclature**

- \( b \) A constant related to the affinity of the binding sites (L/mg)
- \( C_e \) Unadsorbed dyestuff concentration at equilibrium (mg/L)
- \( C_o \) Initial dyestuff concentration (mg/L)
- \( K_F \) Freundlich constant indicating adsorption capacity ((mg/g)/(L/mg)^{1/n})
- \( K_i \) Intraparticle diffusion rate constant (mg/g.min^{1/2})
- \( k_1 \) Pseudo first order kinetic rate constant (1/min)
- \( k_2 \) Pseudo second order kinetic rate constant (g/mg.min)
- \( q_e \) Adsorbed amount per unit mass of adsorbent (mg/g)
- \( q_{e,cal1} \) Calculated adsorbed amount per unit mass of adsorbent from pseudo first order kinetic model (mg/g)
- \( q_{e,cal2} \) Calculated adsorbed amount per unit mass of adsorbent from pseudo second order kinetic model (mg/g)
- \( q_{e,exp} \) Experimental adsorbed amount per unit mass of adsorbent (mg/g)
- \( q_t \) Adsorbed amount per unit mass of adsorbent at any time (mg/g)
- \( Q^o \) Maximum monolayer coverage capacity of adsorbent (mg/g)
- \( 1/n \) Freundlich constant indicating adsorption intensity

**References**


Phosphorus Recovery from Waste Activated Sludge: Comparison of Microwave Treatment and Ozonation in Acidic Environment

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Keywords: Phosphorus recovery; sludge ozonation; microwave treatment

1. Introduction

Activated sludge process has been employed to treat a wide variety of wastewater. Activated sludge has a content rich in phosphorus which is an essential element for living organisms. So, recovery of phosphorus from waste activated sludge as $\text{NH}_4\text{MgPO}_4\cdot6\text{H}_2\text{O}$ or $\text{CaPO}_4$ is a good alternative. However, disintegration of bacterial cell for the release of phosphorus is the most challenging step. It should be efficient, economical and applicable. In this study, microwave treatment, ozonation and acidic pretreatment combined with ozonation were applied to enhance phosphorus recovery from excess sludge and results were compared to reach most efficient process.

2. Material Methods

Sludge disintegration experiments were carried out to study the relationship between treatment and phosphorus recovery. Before ozonation and microwave treatment, acidic treatments were applied to the sludge with 6 N $\text{H}_2\text{SO}_4$. Ozone gas given into 30 and 60 minutes of contact time to the sludge for ozonation. The microwave treatment was applied to the sludge samples for 15 min at 95°C and supplied power of 1600 W. $\text{PO}_4^{3-}$, $\text{NH}_4$, COD, TSS and VSS were determined on Standard Methods (APHA et al., 20\textsuperscript{th} edition). Digestion for total phosphorus measurement were studied according to EPA Method 3052. Mg and Ca were measured by atomic absorption spectrometry. Results of experiments were analyzed with SPSS 23.

After recovery processes; supernatant had been taken from sludge and if it is necessary $\text{MgCl}_2\cdot6\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{SO}_4$ solutions added to achieve $\text{Mg:PO}_4^{3-}:\text{NH}_4$ molar ratio as 1:4:1 as mentioned in Bi et al.(2014). Different alkaline pH conditions in the range of 8.5 – 11.5 were chosen to check Mg and Ca amounts in struvite precipitates (Figure 1).

![Figure 1. Struvite precipitates obtained with different pH conditions](image-url)
3. Results and Discussion

The results of the batch experiments are given in Figure 2 and 3. Sludge solubilization was nearly the same for all methods (around 27%) whereas phosphorus concentration in the bulk liquid of the microwave treatment, ozonation and acidic treatment combined with ozonation experiments were 57.6, 10.52 and 20.28 mgPO₄³⁻/gTSS, respectively. The PO₄³⁻ release percentage in microwave treatment was significantly higher than ozonation and acidic treatment combined with ozonation (p=0.025 and p=0.009).

PO₄³⁻ release was inconspicuous in ozonation without acidic pretreatment experiments while concentration of soluble total phosphorus were increasing with ozonation (Figure 4). As mentioned in Saktaywin et al. (2005) this might be caused by the transmission of internal polyphosphates in PAOs into liquid phase. Dominated group in all struvite precipitation experiments was CaPO₄ with a molar ratio Ca/Mg as around 3:1.

References

Characterization and Treatability of Alkyd Resin Production Wastewater

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Keywords: Alkyd resin production wastewater, esterification, air stripping, acid cracking, strong wastewater

Abstract

In this study, alkyd resin production wastewater characterization and pretreatment of wastewaters for safe storage, toxics removal and strength reduction were realized. Wastewaters originating from the production were strong containing 23-40 g/L COD. Wastewater strength varied with raw materials and products as well as with the amount of wastewater produced. Air stripping tested as a first stage of treatment proved to be efficient reducing COD up to 40% removing solvent residues and volatile matter and increasing the BOD₅/COD ratio 0.57 of raw wastewater to 0.70. The disadvantage of the process is emission of volatiles to air which cannot be captured by alkaline water. Acid cracking process made use of acid character of wastewater which has been enhanced by FeCl₃ addition provided additional 10-33% COD removal which made up an overall COD removal up to 60%. Coagulation-flocculation with FeCl₃ or alum worked better following aeration and acid cracking and increased COD removal with an additional 25%. Saponification using CaCl₂ and BaCl₂ indicated a reuse possibility while COD removal of the process was limited.

1. Introduction

Industrial pollution which is posing significant adverse effects on the environment requires frequently a case by case evaluation for effective control. This is particularly valid for those industries producing toxic and/or concentrated wastewaters. Such cases often arise for chemical industries which have a great spectrum of products manufactured using a variety of processes from which toxic or otherwise hard to deal waste streams originate. As a consequence, scientific literature is rich in this area. There are a number of studies for the characterization and handling of strong wastewaters of organic nature, originating from organic chemicals industry as well as from a variety of other sources. Polyester manufacturing wastewaters (Meriç et al. 1999) textile printing wastewaters (Kabdaşlı et al. 2000), painting wastewaters (Kim et al. 2000) semiconductor wastewaters (Ling et al. 2003), oily wastewaters (Libralato et al. 2008), are examples of such studies. Alkyd resin production, on the other hand, is one of the most common processes which also yields highly polluted and toxic wastewaters yet studies for waste control for this industry are rather scarce. Alkyd resin is the main ingredient of solvent-based paints and has several other uses. Alkyd resin production is realized worldwide on varying scales of plant capacities from small workshops to large integrated chemical plants. The wastewaters originating from the industry are concentrated having 20 – 40 g/L COD and contain toxic compounds such as solvents. The wastewaters exhibit a significant treatment demand before being discharged into joint treatment systems. On the other hand, the processes planned for the treatment of the industry are needed to be applicable by relatively small enterprises.
This study attempts to evaluate the alkyd resin production processes, to define waste streams, their characterization and to conduct treatability studies in the context of reducing wastewater strength and removing the compounds that may inhibit or interfere with joint treatment systems embodying biological treatment. The process analysis and wastewater characterization are based on an alkyd resin production plant which is housed in an integrated paint production factory located near Istanbul.

2. Material Methods

2.1. Wastewater production and characterization
Alkyd resins are a sort of synthetic resin which are produced through condensation reaction of polyalcohols and poly-functional organic acids. The process can be realized by using either fatty acids or fats. If fats are starting material a pre-processing is needed to convert the fats to monoglycerides. This step is realized by reacting the fats with a polyalcohol such as glycerol.. This reaction is termed alcoholysis. After alcoholysis or if the fatty acids are starting material a poly-condensation reaction which is basically an esterification process is employed to produce alkyd resins. An esterification reaction is combination of a carboxylic acid and alcohol to yield an ester and water. The produced water in this reaction is the main source of wastewater from the process. Solvents are also used in the esterification process to remove water. The amount of wastewater originated from alcoholysis process was quite low and determined to be around 0.3 L/ton of production. This waste stream was concentrated having COD values of 300 – 400 g/L and was classified as hazardous waste. The main wastewater source is esterification process and the amount of wastewater as mentioned above changes depending on the sort of product. Our evaluation for a variety of products indicated a range 10 – 20 L of wastewater per ton of product, however, the amount was frequently closer to the upper end. For the characterization of esterification wastewater samples were taken for productions of different character and results are presented in Table 1.

Table 1. Character of wastewaters of esterification process

<table>
<thead>
<tr>
<th>Sample</th>
<th>COD [g/L]</th>
<th>TOC [g/L]</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>35 – 38</td>
<td>8 – 9</td>
<td>2.0 – 2.5</td>
</tr>
<tr>
<td>II</td>
<td>23 – 24</td>
<td>6 – 7</td>
<td>2.0 – 2.5</td>
</tr>
<tr>
<td>III</td>
<td>35 – 40.5</td>
<td>8 – 12</td>
<td>2.0 – 2.5</td>
</tr>
</tbody>
</table>

Other parameters measured were chloride, sulfate, oil and grease, and suspended solids. Suspended solids concentration was 70 mg/L while all others were below 10 mg/L. Therefore, acidity and organic matter were the main parameters characterizing the wastewater. The BOD5 of Sample II was measured and BOD5/COD ratio was found as 0.57 indicating a moderately biodegradable wastewater. COD of samples was variable. COD/TOC ratios varied between 3.75 and 4.4 indicating this variability was also affected by structural differences. However, the amount of wastewater was another determining factor of wastewater strength (Çakır, 2009). The only literature data we could reach was the study of Schwingel de Oliveira et al. (2007) where wastewater strength was given as 80750 mg/L COD and 33600 mg/L TOC.
2.2. Planning of treatability study
The wastewaters, although BOD5 value indicated biodegradability, were strong and required to be diluted before biological treatment. However, dilution requirement was high and could be facilitated if the wastewater was partially treated. On the other hand, the wastewater contained solvents which were toxic and needed to be removed before biological treatment. Preliminary experiments indicated the presence of a volatile fraction in the wastewater. Removal of volatile fraction is important for toxic control as well as for safety of temporary storage of the wastewater. Aeration is a simple means for removing solvents and volatile substances and proved to be an efficient process as in the case of textile printing wastewater treatment (Kabdaşlı et al. 2000). Hence, aeration is planned as the first step of treatment. Further treatment steps are also planned as low cost, physical-chemical processes that can be realized even at small facilities. Acid cracking supported with ferric chloride (FeCl₃) addition was applied considering already low pH of wastewater. Coagulation-flocculation with the use of alum or ferric chloride was applied in place of or in addition to acid cracking. As an alternative treatment and as a means of recovery saponification using calcium and barium salts was also tested.

2.3. Experimental procedure
Aeration was realized in Erlenmeyers into which air was feed through diffusers. The system was operated either open to the atmosphere or connected to scrubbers containing aqueous alkaline solution. Three gas washing bottles connected in series were used for this purpose. Aeration was accomplished both at pH 2.0 (original pH of the samples) and at pH 7.0. Air flow was varied between 1.6 – 6.4 m³/L×h where L is the aerated wastewater volume. 1.6 m³/L×h air flow is denoted by Q. Acid cracking experiments were run in a Jar-Test with 15 minutes flash-mixing, 15 minutes slow mixing and 2 hours separation sequence. The experiments were conducted at pH 2.0 – 2.5 and with FeCl₃ dosage of 1000 mg/L at the beginning and 10 mg/L non-ionic polyelectrolyte addition 1 – 2 minutes before the slow mixing began. Coagulation-flocculation experiments were carried out again in a Jar-Test with the same sequence and timing that of acid cracking. Alum (1000 mg/L) or FeCl₃ (1000 – 1500 mg/L) and polyelectrolyte (10 mg/L) were used. pH of the solution was adjusted to 6.0 – 6.5. Saponification was realized using either CaCl₂ or BaCl₂ addition with flash-mixing and settling at pH 10.0.

All analyses were performed as defined in Standard Methods (1998) except for COD measurements. COD was determined by the open reflux titrimetric method according to ISO 6060 (1986). TOC was monitored on a Tekmahr-Dorhmann Apollo 9000 model carbon analyzer. pH measurements were made with Orion 720A+ model pHmeter.

3. Results and discussion
3.1. Aeration
Aeration experiments were conducted for four different air flows and for two different pH values. The two pH values employed were pH 2.0 – 2.5 and pH 7.0. The aim was to differentiate the fractions; volatile, non-polar substances that are removable by aeration being practically independent of pH and polar fraction that can be volatilized in unionized (molecular) form at low pH values. Experiments were carried out in order to determine the aeration duration. The aeration time was extended to 148 hours in the experiments. The results indicated that COD
removal practically ceased at 32 hours. Figure 1(a) delineates COD abatements obtained for Sample I during aeration with an air flow (Q) of 1.6 m$^3$/L×h.

As seen from Figure 1, COD abatement was realized at a great extent until 12 hours, and only a slight difference existed beyond the aeration time of 12 hours for both pH values tested. COD removals at acidic pH value were more rapid than those of pH 7.0 until 12 hours, but ultimate COD removals were very close to one another implying that majority of the volatile fraction was of apolar nature. The solution pH which remained constant during the entire aeration period, further testified this conclusion. COD removal efficiencies at the end of aeration time of 32 hours at pH 2 and 7 were measured as 37 and 38%, respectively. COD/TOC ratio may be taken as a measure of compositional homogeneity of the sample, therefore TOC changes were monitored in parallel with COD during aeration experiments (Fig. 1(b)). COD/TOC ratio was measured at time zero of aeration as 3.73 and 4.0 for pH 2 and 7, respectively. COD/TOC ratio fluctuated between the range of 3.77 and 3.11 for aeration at pH 2, and 4.3 and 3.16 for aeration at pH 7 within the first 12 hours. These ratios were 3.11 and 3.24 at the end of 12 hours and further decreased to 2.8 and 3.06 at the end of 32 hours for pH 2 and 7, respectively. These significant reductions in COD/TOC ratios can be attributed to changes in the composition of the sample during aeration. The results of aeration experiments obtained for pH 2.0 – 2.5 and for the end of 32 hours are tabulated in Table 2 for varying aeration intensities.

Table 2. Results of aeration experiments conducted on varying air flows (Q = 1.6 m$^3$/L×h)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Aeration Intensity</th>
<th>COD Initial [mg/L]</th>
<th>COD Final [g/L]</th>
<th>COD Removal [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Q</td>
<td>31000</td>
<td>19000</td>
<td>39</td>
</tr>
<tr>
<td>I</td>
<td>4Q</td>
<td>31000</td>
<td>19000</td>
<td>39</td>
</tr>
<tr>
<td>II</td>
<td>Q</td>
<td>23000</td>
<td>19570</td>
<td>15</td>
</tr>
<tr>
<td>II</td>
<td>2Q</td>
<td>23000</td>
<td>16050</td>
<td>30</td>
</tr>
<tr>
<td>III</td>
<td>Q/8</td>
<td>40310</td>
<td>31370</td>
<td>21</td>
</tr>
</tbody>
</table>
As can be seen from Table 2, process efficiencies depend on character of the wastewater. Aeration intensities did not affect the efficiency for Sample I, but significantly affected the process performance for Sample 2, also a very low aeration intensity would be effective for the case of Sample III. Since both raw materials used in the production and process characteristics vary depending on the product, the wastewater character and the response of wastewaters to aeration will vary. This work helps to define a framework for the process based on the main parameters. Air stripping as a simple aeration or as more efficient tower designs has been used for volatile control. Although wastewater characters are different there are applications to strong organic wastewaters containing volatile organic matter. Kabdaşlı et al. (2000) applied aeration to textile printing wastewaters which contained solvents and other volatile material. COD of wastewater was 47 – 49 g/L. Aeration provided 38 – 40 % COD removal. Tünay et al. (2010) obtained up to 26% COD removal by aeration of latex-based paint wastewaters.

BOD₅ measurements on Sample II undergone aeration for 32 hours at pH 2.0 and an aeration intensity of 2Q resulted in a BOD₅/COD ratio of 0.70. Considering the BOD₅/COD ratio of 0.57 for the raw Sample II aeration could be evaluated as a process removing the solvents, other toxic or otherwise hard to treat components yielding a relatively diluted wastewater which is more amenable to biological treatment. However aeration process requires a well worked optimization for the best results .The main disadvantage of aeration is the stripping of solvents and other materials directly off the air which causes air pollution. Therefore, a test was planned to evaluate if a part of volatile off gases could be captured by using an alkaline aqueous solution. The experiment was conducted using Sample I at pH 2.0 and with an air flow of Q. COD removal at the end of 32 hours was found as 32%. Result of the experiment was evaluated on the mass of COD basis, and captured COD in scrubbers was determined as 6.6 % removed COD. This amount can be interpreted as non-solvent volatile components removed from the sample. Solvent removal may be carried out using special solutions, oils, or special absorbers.

3.3. Acid cracking with FeCl₃
Acid cracking experiments were run on both raw and aerated samples. Results of experiments are summarized in Table 3. As seen from the table, COD removals were between 10 – 21 %. These figures were lower than those of aeration pretreatment. Even lower efficiencies were obtained for aerated samples except for Sample I for which 33 % acid cracking and overall (aeration + acid cracking) roughly 60% COD removal were reached. For Sample 1 COD/TOC ratios were found for aerated and acid cracking of aerated samples as 2.8 and 2.2, respectively. These figures again indicated a structural change in the wastewater. Biodegradability however, remained at the same level as indicated by BOD₅/COD ratio of 0.72 for Sample II. Acid cracking process was effective in several cases as oily and paint production wastewaters. Kabdaşlı et al. (2012) obtained up to 95 % COD removal by acid cracking for wastewaters originating from water-based paint production with latex binder with COD values up to 16 g/L.
Table 3. Results of acid cracking experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial [mg/L]</th>
<th>Final [mg/L]</th>
<th>Removal [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>31000</td>
<td>24480</td>
<td>21</td>
</tr>
<tr>
<td>I</td>
<td>19000</td>
<td>12800</td>
<td>33(59)*</td>
</tr>
<tr>
<td>II</td>
<td>23000</td>
<td>19350</td>
<td>16</td>
</tr>
<tr>
<td>II</td>
<td>19570</td>
<td>17330</td>
<td>12(25)*</td>
</tr>
<tr>
<td>II</td>
<td>16050</td>
<td>13960</td>
<td>13(40)*</td>
</tr>
<tr>
<td>III</td>
<td>40310</td>
<td>33750</td>
<td>16</td>
</tr>
<tr>
<td>III</td>
<td>31730</td>
<td>28590</td>
<td>10(29)*</td>
</tr>
</tbody>
</table>

*overall COD removal

3.4. Coagulation and flocculation
Coagulation and flocculation experiments were performed on Sample III using either FeCl₃ or alum with dosages varying between 1000 and 1500 mg/L. These experiments yielded up to 15 % COD removals. However, the process provided better results for acid cracking effluent and 25 and 26 % COD removals obtained with 1000 mg/L FeCl₃ and alum, respectively. The process, although not highly efficient, increased the total dilution of highly concentrated Sample III to 47 % together with aeration and acid cracking.

3.5. Saponification
Saponification was tested as an alternative process and as a means of recovery using calcium and barium salts at pH 10 on aerated Sample II. COD of aerated Sample II could be reduced 5 and 7 % using barium (6.7 g/L BaCl₂) and calcium (3.4 g/L CaCl₂), respectively. The separated solid phase are likely fatty acids combined as metal soaps.

Conclusions
This study attempted to analyze the production processes and wastewater production of alkyd resin manufacturing. The main wastewater source is esterification process with wastewater flow ranging between 10 and 20 L/ton product. The wastewater is strong containing 23 – 40 g/L COD. The strength depends on raw materials and products as well as wastewater production. Wastewater character is also variable as reflected by COD/TOC ratio which changes in the interval 3.75 – 4.4. The wastewater is moderately biodegradable as indicated by BOD₅/COD ratio of 0.57. Relatively easy to use physical-chemical pretreatment alternatives were tested to remove toxicity, increase the biodegradability, provide safe storage and dilute the wastewater. Aeration as a first step treatment proved to be useful, removing solvents and other volatiles increasing biodegradability and providing a significant dilution by reducing the COD up to 40%. Removal efficiencies depend on wastewater character, composition as well as on aeration intensity. The drawback of the process is the need of capturing volatile fraction for which alkaline scrubbing could retain 6% of volatilized COD. Acid cracking performance was found variable on raw and aerated samples. Aerated sample responses were between 10 – 33 % COD removal and at the highest removal, aeration plus acid cracking, COD removal efficiency reached 60%. Coagulation and flocculation worked better on samples pretreated with aeration.
and acid cracking with a COD removal around 25%. Precipitation with calcium and barium salts, although COD removal are limited, may provide recovery of fatty acids.

References


Towards Efficient Use of Municipal Wastes and Wastewater for Energy Recovery in Eco-cities

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Keywords: energy recovery, anaerobic processes, wastewater segregation, OFMSW, CHP

Abstract

Eco-cities are expected to be established in line with sustainability concept for the sake of energy minimization which in turn leads to less greenhouse gas emissions. Waste and wastewater management issues should not be underestimated while designing eco-cities. Not only environmental merits; but also, economic contributions could be provided accordingly. In this paper, energy recovery calculations and estimations from municipal solid wastes (MSW) and domestic wastewater that will arise from a fictitious eco-city in Istanbul-Turkey with a proposed population of 100,000 will be briefly discussed. The results indicate that there is an important energy recovery potential from organic fraction of municipal solid waste (OFMSW) and domestic wastewater. The overall energy recovery as electricity and heat is calculated as 31 MWh/day, and it roughly corresponds to electricity demand of 1600 households.

1. Introduction

Depletion of fossil sources has forced humans to find new energy sources in the last decades. Renewable energy sources such as wind, solar and geothermal have become popular in this respect. Renewable energy sources, known as environmentally friendly sources as greenhouse gas emissions are not released during energy production from these sources. Biomass energy, known as bioenergy, is another renewable source extracted from organic molecules or residues. The residuals can be either in liquid (wastewater) or solid (solid waste) forms. Organically rich materials are counted as energy-rich materials and their energy content can be recovered via biochemical reactions. This paper addresses the recent technologies and methods to recover the energy content of “residuals” of a society.

An important question arises at that point. What would be the methods to efficiently recover energy content from “residuals”? The key point is segregation of energy-rich streams in both wastewater and solid waste. Sorting at source should be performed to separate organic and inorganic municipal solid waste (MSW) fractions. Valorization of organic fraction of municipal solid waste (OFMSW) will be discussed in this paper. Issues on energy and material recoveries will be evaluated for this purpose. A proposed management strategy for OFMSW is given in Figure 1.

On the other hand, ecological sanitation (ECOSAN) is the common implementation to segregate wastewater systems which have different properties in terms of quantity and quality.
Blackwater is the fraction of wastewater that can be recovered. Anaerobic processes should be applied for energy recovery from blackwater as well as OFMSW.

![Diagram of OFMSW management strategy (Møller et al., 2009)](image1)

Biogas is the most significant product of anaerobic processes that could be utilized in combined heat and power plants (CHP) to produce electricity and heat. Energy and material recoveries from blackwater is schematically shown in Figure 2.

![Diagram of Valorization of blackwater (Verstraete et al., 2009)](image2)

### 2. Material Methods

#### 2.1 Wastewater management in the eco-city

There are many alternatives in wastewater treatment and reuse that need to be investigated for selecting the best site-specific option. Eco-city concept in wastewater management refers smaller foot-print, lower energy consumption with sludge production, and higher energy recovery compared to old school technologies. Anaerobic wastewater treatment is suitable especially in terms of energy recovery. Upflow anaerobic sludge blanket (UASB) is one of the commonly applied anaerobic wastewater treatment method. The main constraint about UASB and other anaerobic treatment relates to the strength of wastewater that should be kept at a certain level to make the anaerobic treatment feasible. For this study, it is estimated that the strength of the wastewater can be kept at the desired level. Greywater, which lowers the strength of the wastewater, will be separated from the blackwater and recycled. It is also expected that the infrastructure of the eco-city will be proper enough to prevent any leakages; thus, the wastewater will not be diluted by groundwater or stormwater.
In Turkey, the average daily water consumption can be taken as 120 L/ca/day, however this value can be increased to 150 L/ca/day to be on the safety side. It should be noted that water consumption and wastewater generation are different terms and wastewater generation can be considered as 80% of the water consumption. Therefore, it is accounted as 120 L/ca/day. The reuse alternative for greywater is not within the scope of this paper; but, water savings through greywater should be regarded in wastewater generation calculations. Greywater generation can be taken as ~50 L/ca/day excluding laundry wastewater as it is not generally preferred for reuse especially for hygienic purposes. Thus, the daily unit wastewater amount per capita and the corresponding total amount arising from the fictitious eco-city that will be treated in the wastewater treatment plant (WWTP) will be 120 L/ca/day–50 L/ca/day = 70 L/ca/day and daily amount will be 100,000 x 70 L/ca/day = 7000 m$^3$/day.

Wastewater characterization is the next step in designing of a WWTP. Turkish Regulation of Technical Methods in Wastewater Treatment Plants (2010), states the unit pollution loads for each design parameter. Hence, the pollutant loads of the wastewater without any stream segregation will be calculated as follows;

- Chemical oxygen demand (COD) load = 100,000 x 110 g/ca/day = 11,000 kg COD/day
- Biochemical oxygen demand (BOD5) load = 100,000 x 55 g/ca/day = 5500 kg BOD5/day
- Suspended solids (SS) load = 100,000 x 60 g/ca/day = 6000 kg SS/day
- Total nitrogen (TN) load = 100,000 x 7.5 g/ca/day = 750 kg TN/day
- Total phosphorus (TP) load = 100,000 x 1.2 g/ca/day = 120 kg TP/day

It should be noticed that the influent loads at the WWTP will be different than the calculated values given above as greywater will be separated from the wastewater to be reused. It is obvious that greywater is comparatively of lower strength than blackwater; therefore, the wastewater will have higher strength after greywater segregation. Influent wastewater characterization excluding greywater is tabulated in Table 1 which also gives the range of raw greywater parameters with the typical values to be considered in the design work.

### Table 1. Characterization of raw greywater and wastewater excluding greywater

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Raw greywater characterization (mg/L) (Karahan, 2009)</th>
<th>Wastewater characterization excluding greywater (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>150-400 (225)</td>
<td>1411</td>
</tr>
<tr>
<td>BOD</td>
<td>85-200 (111)</td>
<td>706</td>
</tr>
<tr>
<td>SS</td>
<td></td>
<td>779</td>
</tr>
<tr>
<td>TN</td>
<td>4-16 (10)</td>
<td>100</td>
</tr>
<tr>
<td>TP</td>
<td>0.5-4.0 (1.5)</td>
<td>16</td>
</tr>
</tbody>
</table>

The disposal of excess treatment sludge is another issue to be discussed. The management of the sludge should be coherent with the eco-city concept. The sludge production in anaerobic treatment is generally taken as 5% of the input COD load. Therefore, the sludge production on dry matter basis in the WWTP will be 7000 m$^3$/day x 1411 g COD/m$^3$ x 0.05 x 365 days/year = 180
t/year. If the sludge is dewatered and the total solids content is elevated to 25%, the final amount will be 180 t/year × 0.25 = 720 t/year.

COD concentration is an indicator of the energy content of the wastewater. It is converted to biogas under anaerobic conditions where the conversion ratio is given as 0.35 m³ of CH₄ per kg of COD at standard conditions (0°C and 1 atm). In the fictitious eco-city, UASB is proposed to treat wastewater and a CHP plant will be constructed to produce energy from generated biogas. If the COD conversion ratio is taken as 60% during the treatment process, daily biogas generation in the WWTP can be calculated as 7000 m³/day × 1411 g COD/m³ × 10⁻³ g/kg × 0.35 m³ CH₄/kg COD × 0.6 × (100/55) × 365 days/year = 1,376,216 m³ biogas/year (assuming 55% of biogas is methane). Energy equivalence of biogas; 1,376,216 m³ biogas/year × 5 kWh/m³ biogas = 6,881,080 kWh/year. The installed capacity of the CHP plant is calculated as 6,881,080 kWh/year / (24 × 365) = 786 kW by assuming that the energy production will be continuous all throughout the year. The energy requirement, especially in terms of heat in winter, should not be missed. For simplification purposes, 25% of the total generated energy can be counted as the energy requirement of the treatment process. Efficiency of new generation gas engines can be taken as around 85%, among which 35% is electrical energy and 50% is heat energy. Thereby, the total energy potentials can be recovered accordingly;

Electrical Energy: 786 kW × 0.35 × (1 – 0.25) = 206 kWₑₑ

Heat Energy: 786 kW × 0.50 × (1 – 0.25) = 295 kWₑₑ

2.2 Solid waste management in the eco-city

Not only considering the energy recovery issue; but also building a municipal solid waste (MSW) management system for an area entails the estimation of solid waste generation. The unit MSW generation data for Istanbul is taken from the Turkish Statistical Institute (TUIK, 2014). The data for 2014 is given as 1.16 kg/ca/day. Thus, the total MSW generation will be 100,000 × 1.16 kg/ca/day × 365 days/year = 42,340 t/year. The latter step is the estimation of waste characterization which determines the capacities and foot-prints of waste treatment facilities such as landfill, composting and recovery units. ISTAC Inc., the contractor company for waste management in Istanbul, had a waste characterization study in 2012. The recent study implies that half of the generated waste is organic waste and this fraction is mainly originated of kitchen waste. The results of the study are given in Table 2.
Table 2. Solid waste characterization in Istanbul (Ozturk, 2016)

<table>
<thead>
<tr>
<th>Component</th>
<th>% (on wet basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper-cardboard</td>
<td>11.33</td>
</tr>
<tr>
<td>Glass</td>
<td>3.94</td>
</tr>
<tr>
<td>Pet</td>
<td>1.45</td>
</tr>
<tr>
<td>Plastic bag</td>
<td>9.55</td>
</tr>
<tr>
<td>Plastic</td>
<td>2.37</td>
</tr>
<tr>
<td>Metal</td>
<td>1.15</td>
</tr>
<tr>
<td>Organic waste</td>
<td>50.18</td>
</tr>
<tr>
<td>Electrical and electronical waste</td>
<td>0.18</td>
</tr>
<tr>
<td>Hazardous waste</td>
<td>0.32</td>
</tr>
<tr>
<td>Tetra Pak</td>
<td>0.68</td>
</tr>
<tr>
<td>Textile</td>
<td>5.62</td>
</tr>
<tr>
<td>Diaper</td>
<td>4.77</td>
</tr>
<tr>
<td>Yard wastes</td>
<td>1.18</td>
</tr>
<tr>
<td>Other combustible wastes</td>
<td>6.10</td>
</tr>
<tr>
<td>Other incombustible wastes</td>
<td>1.18</td>
</tr>
</tbody>
</table>

Waste segregation at source is the key factor in building up a successful waste management system and for recovering energy. For developing countries, such as Turkey, dual collection is the best option to separate organic waste and package waste (paper, glass, metal, etc.). Nevertheless, some inevitable losses usually occur during waste collection and handling processes. The main sources for losses are referred below. It should be noted that the given ratios are quite sensitive to site and applied techniques.

- Losses in dual collection: ~20%
- Losses during transportation and storage: ~10%
- Losses in treatment process: ~10%

By using the given ratios given above, the waste input for the biomethanization facility is calculated as 14,811 ton/year. Similarly with the wastewaters, energy recovery from organic wastes by means of anaerobic processes is the most favourable choice to obtain the energy content of the waste. Hereby, for the fictitious eco-city of this study, the produced biogas in the biomethanization facility will be converted to energy at the CHP plant. Kitchen waste, yard wastes and treatment sludge generated in the WWTP will be digested in this facility. The handled waste components and their corresponding amounts are given in Table 3.
Table 3. Wastes to be treated in the biomethanization facility

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount (t/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kitchen waste</td>
<td>13,768</td>
</tr>
<tr>
<td>Yard wastes</td>
<td>324</td>
</tr>
<tr>
<td>Treatment sludge*</td>
<td>720</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>14,811</strong></td>
</tr>
</tbody>
</table>

* The amount of sludge cake having 25% of total solids content

There are various values cited in literature for biogas production via anaerobic digestion of different wastes. Mata Alvarez (2003) suggested that 100 m$^3$ of biogas can be produced per ton of digested organic fraction of municipal solid waste (OFMSW). In another study, the biogas yield of the digestion of OFMSW was given in the range of 60-200 m$^3$ biogas/ton waste (Li et al., 2011). All these studies on the digestion of OFMSW point out that the impurities of OFMSW have a huge impact on the biogas yield. Since organic waste is the main input for the biomethanization facility, the governing waste component in the operation will be organic waste rather than yard wastes and treatment sludge. In the light of the above-referred information, the overall biogas yield was taken as 150 m$^3$ biogas/ton digested waste in this study. It is anticipated that this value will not be lower by the help of high dual collection efficiency in the eco-city. As a result, the annual biogas production in the 14,811 ton/year x 150 m$^3$ biogas/ton waste = 2,221,825 m$^3$ biogas/year and the energy equivalence of biogas is 2,221,825 m$^3$ biogas/year x 5 kWh/m$^3$ biogas = 11,109,125 kWh/year.

The energy requirement of biomethanization facilities is a well-known and there is no doubt that the requirement is higher in cold seasons. It is not so easy to estimate the energy requirement of a biomethanization facility because the used technology and the climate affect it substantially. For a biomethanization facility treating 15,000 ton waste/year, the energy consumption of the plant itself was mentioned as 25% of the total energy production (Mata-Alvarez et al., 2000). The installed capacity of the CHP plant is calculated as 11,109,125 kWh/year/ (24 x 365) = 1268 kW by assuming that the energy production will be continuous during the year. In summary, related electricity and heat energy production capacities are further calculated by using the same ratios given above accordingly;

Electrical Energy: 1268 kW x 0.35 x (1 – 0.25) = 333 kW$_{el}$
Heat Energy: 1268 kW x 0.50 x (1 – 0.25) = 476 kW$_{heat}$

3. Results and Discussion

- Total population in the fictitious ABC eco-city = 100,000 people
- Daily wastewater generation = 100,000 x 120 L/ca/day = 12,000 m$^3$/day
- Daily wastewater will be treated in the WWTP = 100,000x70 L/ca/day = 7,000 m$^3$/day
- Annual MSW generation = 100,000 x 1.16 kg/ca/day = 42,340 t/year
- Annual MSW will be digested in the biomethanization facility = 13,768 t/year kitchen waste + 324 t/year yard wastes + 720 t/year treatment sludge = 14,811 t/year
- Total installed capacity for the CHP plant = 786 + 1268 = 2054 kW ~ 2.0 MW
- Total electrical energy production capacity = 206 + 333 = 539 kW$_{el}$
- Total heat energy production capacity = 295 + 476 = 771 kW$_{heat}$
539 kWel energy corresponds to ~4700 MWh/year of electrical energy. If the average electricity consumption is taken as ~3000 kWh/household/year, which is the average value for Turkey (Url-1), this energy supplies the energy demand of ~1600 households (assuming 4 people in each household; this value is almost equal to 6400 people addressing around 6.4% of the fictitious eco-city population). In addition to electricity, the produced heat can be used as a supplementary source for producing hot water and for heating the buildings.

It is possible to build one CHP plant which receives biogas from both the WWTP and the biomethanization facility. The results reveal that recovery of domestic wastewater and OFMSW have an important energy potential, and energy can be recovered by applying appropriate technologies. This approach can be an environmentally friendly way to eliminate the negative impacts of wastewater and MSW management while contributing to saving of fossil sources.

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Sustainable water management in eco-cities: wastewater reuse and rainwater recycling

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Keywords: eco-cities, greywater, rainwater harvesting, wastewater, water gain.

Abstract

Cities of the future need to be planned as eco-cities intending efficient water and energy use. In that sense, alternative water resources are searched. Among the potential ones, the two popular ones are greywater reuse and rainwater harvesting. The study refers to the basic advantages of these water resources and to the driving factors and main parameters involved in the estimation and calculation of their potential quantity to be safely used in households. A rough calculation on the daily amount of both resources are given for a fictitious eco-city of 100,000 population located in Istanbul-Turkey. As such, at least 40% water gain is shown to be possible with utilizing greywater arising from shower and taps and rainwater harvesting through the roofs with a long-term average annual precipitation value of around 800 mm.

1. Introduction

Supplying adequate amount of water in acceptable quality is one of the outstanding issues of future especially in urban cities where the population density is comparatively high. This reality urges people to find new and alternative water resources for the cities of future. New residential areas known as eco-cities usually intend efficient water and energy management (Url-1). Thus, searching alternative water resources for the cities of future is a common current issue that aims

- to reduce the consumption of clean and limited water resources,
- to reduce pollution of receiving water bodies by partly preventing the discharge of wastewater,
- to respond to high water demand especially in crowded residential areas and cities, and
- to cope with the effects of climate change (Gleick, 2000; Novotny, 2009; Novotny, 2011; Novotny, 2013).

Alternative water resources will be briefly discussed and some rough calculations and estimations on the water gain through these proposed resources will be mentioned for a planned eco-city ABC in Istanbul. First alternative is wastewater reuse for a variety of uses. Today's advanced technology of wastewater treatment like any of the separation processes are suitable to provide better quality effluents to be reused in various human-related activities like irrigation, energy recovery, etc. (Asano et. al., 2007). Second alternative resource has a growing trend nowadays; namely, greywater use especially for flushing toilets. Greywater is defined as wastewater generated from wash hand basins, showers and baths, which can be recycled on-site for uses such as toilet flushing, landscape irrigation and constructed wetlands. It often includes discharge from laundry, dishwashers and kitchen sinks. It differs from the discharge
of toilets which is designated sewage or blackwater that contains human waste (EPA, 2013; Waterscan, 2013).

Third one is an already known technology for centuries; however, it has become famous especially in regions facing water scarcity. It is rainwater harvesting expressed as storage of rainwater for reuse before it reaches the aquifer. This renewable resource can be used for garden/green area irrigation, for livestock, and for indoor heating for buildings etc. Rainwater harvesting systems in houses are preferred as micro use (SSWM, 2013) and, in open area for land irrigation as macro use.

This emerging topic aims to highlight the so-called alternatives which will gain more interest in the coming years as climate change will have more pronounced effects. All the three alternatives bear advantages and disadvantages; however, in this study, greywater recycling and rainwater harvesting options will be referred.

2. Material Methods

Population is the governing parameter for calculating the quantity of greywater to be recycled and reused; whereas, the total surface area and roof structures of the buildings of the planned eco-city are among the driving factors for estimating the water gain through precipitation. Above all, the most important parameter is the frequency and intensity of precipitation regarding rainwater harvesting.

Table 1 shows domestic water consumption types and their corresponding distribution according to different living standards and countries. Important point heading reuse depends on the requirement for potable water in this variety of uses. This is given in Table 2. The values in this table are derived from the previous table. It is for sure that potable water that is necessary in a household forms a minority (4-10%) compared to other uses. Toilet flushing and outdoor use of domestic water that constitutes almost half of the domestic water need do not require potable water and may easily be provided from greywater and rainwater.

### Table 1. Domestic water consumption types and their distribution

<table>
<thead>
<tr>
<th>Domestic Water consumption</th>
<th>% distribution in UK</th>
<th>% distribution in USA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kitchen &amp; drinking</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Bath &amp; shower</td>
<td>20</td>
<td>32.5</td>
</tr>
<tr>
<td>Washing up</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td>Cleaning</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>Toilet flushing</td>
<td>29</td>
<td>26.7</td>
</tr>
<tr>
<td>Outdoor use</td>
<td>35</td>
<td>13.7</td>
</tr>
<tr>
<td>Others</td>
<td>5</td>
<td>5.3</td>
</tr>
</tbody>
</table>

### Table 2. Requirement for potable water in domestic water use

<table>
<thead>
<tr>
<th>Potable water not required</th>
<th>Potable water required</th>
<th>Potable water optional</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toilet flushing: 30%</td>
<td>Drinking/cooking: 4-10%</td>
<td>Bath/shower: 20-35%</td>
</tr>
<tr>
<td>Watering lawn/garden irrigation/cleaning: 20%</td>
<td>Laundry/dishwashing: 15-20%</td>
<td></td>
</tr>
<tr>
<td>50%</td>
<td>4-10%</td>
<td>15-20%</td>
</tr>
</tbody>
</table>
As a general perspective, rainwater is accepted as an alternative water resource; however, apart from its advantages, it also bears some disadvantages. Table 3 summarizes its advantages and disadvantages.

Table 3. Strengths and weaknesses of rainwater harvesting

<table>
<thead>
<tr>
<th>Strengths of rainwater harvesting</th>
<th>Weaknesses of rainwater harvesting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Generally, investment and operational costs are lower compared to other water supply systems.</td>
<td>Reliability of this system is low due to unpredictable precipitation.</td>
</tr>
<tr>
<td>Construction and operation is easier.</td>
<td>It is a selfish solution; it kills the sharing feelings.</td>
</tr>
<tr>
<td>Responsibility of operation in the individual systems belongs to the owner.</td>
<td>Responsibility of operation belongs to the owner. In that sense, it may not be desirable.</td>
</tr>
<tr>
<td>It may be linked with the existing water distribution system.</td>
<td>It may lead to income reduction of the municipality or of the private firms that supply water to the residential sites.</td>
</tr>
<tr>
<td>Adaptation to the system is easy.</td>
<td>Governments have so far not developed any policy regarding this alternative water resource. Thus, public awareness is weak in this issue.</td>
</tr>
<tr>
<td>Negative environmental impacts are lower when compared to other water supply systems.</td>
<td>Tanks and depots may cause a threat to children.</td>
</tr>
<tr>
<td>Obtained water is for no cost.</td>
<td>Tanks and depots may require land.</td>
</tr>
<tr>
<td>Obtained water is near the consumption site.</td>
<td></td>
</tr>
<tr>
<td>Obtained water is of higher quality compared to other water supplies. It may be used without any treatment.</td>
<td></td>
</tr>
<tr>
<td>It helps to protect the existing water resources.</td>
<td></td>
</tr>
<tr>
<td>It may be used with ease under emergency conditions (earthquake, drought, etc.).</td>
<td></td>
</tr>
<tr>
<td>Reduces flooding.</td>
<td></td>
</tr>
</tbody>
</table>

2.1 Water savings through reuse and recycling in eco-cities

2.1.1 Greywater reuse

The most recommended option of reusing greywater is to use it in toilet flushing systems. The applicability of such an option is quite high in the planned eco-cities rather than the already existing ones. The other optional utility area is to use it in the laundries. However, this practice is not widely accepted by public especially in the developing countries.

In Turkey, representing a developing country, the average daily domestic water consumption is 120 L/capita.day; but to be on the safety side; it is taken as 150 L/capita.day in the design work and flow calculations. Domestic wastewater arising daily is accepted as 80% of the water consumed. Thus; it is taken as 120 L/capita.day. 40% of this amount originates from showers, bath and taps. When the wastewater arising from the laundries are excluded, the greywater generation is around 48~ 50 L/capita.day. 90% of this amount may be considered as recyclable greywater after treatment (10% of water will be lost during treatment) which is ~45 L/cap.day. 25-30% of domestic water is used in the toilet flushing systems which accounts to ~40 L/cap.day. As seen from these rough calculations, greywater, excluding wastewater arising from the laundry, can be readily used as toilet flushing water.
Under daily per capita basis

Treated greywater (excluding laundry wastewater) =~ Toilet flushing water need

Greywater consists of detergents, skin oil, hair, skin and scuff particles that can easily be decomposed. In case the greywater is not processed immediately after it is generated, biological degradation process continues with sulphates resulting in an undesired smell. Greywater containing wastewater from the showers, baths and taps are comparatively less polluted. If laundry wastewater is included in the greywater, its polluting parameters will increase in concentration and will necessitate more cost for treatment. Moreover, including kitchen wastewater to the greywater will even increase the treatment costs more. Table 4 shows the raw greywater quality arising from various household fixtures.

Table 4. Raw greywater quality arising from various household fixtures (Karahan, 2009)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Shower, bath, taps</th>
<th>Shower, bath, taps &amp; laundry</th>
<th>Shower, bath, taps, laundry &amp; kitchen wastewater</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg/L)</td>
<td>150-400 (225)</td>
<td>250-430</td>
<td>400-700 (535)</td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>85-200 (111)</td>
<td>125-250</td>
<td>250-550 (360)</td>
</tr>
<tr>
<td>Total P (mg/L)</td>
<td>0.5-4 (1.5)</td>
<td>Not available</td>
<td>3-8 (5.4)</td>
</tr>
<tr>
<td>Total N (mg/L)</td>
<td>4-16 (10)</td>
<td>Not available</td>
<td>10-17 (13)</td>
</tr>
<tr>
<td>pH</td>
<td>7.5-8.2</td>
<td>Not available</td>
<td>6.9-8</td>
</tr>
</tbody>
</table>

Indoor water savings through use of greywater in the fictitious eco-city ABC:

- Total Population = Overall 100 000 people and the settlements will be realized in 4 stages.
- Stage 1= 35 000 capita x 45 L/cap.day= 1 575 m³/day
- Stage 2= 25 000 capita x 45 L/cap.day = 1 125 m³/day
- Stage 3= 15 000 capita x 45 L/cap.day = 675 m³/day
- Stage 4= 25 000 capita x 45 L/cap.day = 1 125 m³/day
- Total water saving via reuse of greywater= 100 000 x 45= 4 500 m³/day

Investment cost of greywater collection and treatment systems vary according to the size of the facility. As the size of the facility increases, the cost will decrease together with the depreciation period. The investment cost of greywater collection and treatment system per flat in a building consisting of 15–20 flats in Turkey is around 600 Euros. This amount may decrease up to 200 euros in facilities with 500 flats. The depreciation period of such system is less than 2 years in a facility with 200 flats. The operation cost of these systems covers energy, repairs, maintenance and routine controls. In a simple facility, 1% of the investment cost can be estimated as the annual operational cost, 4% as maintenance and repair cost. Energy cost for 1 m³ of water use is around 1.5–3 kW (Karahan, 2009).

2.1.2 Rainwater harvesting
Rainwater harvesting is closely linked with annual amount and frequency of precipitation. It is difficult to forecast the regime of precipitation. In regions receiving high precipitation like
1000-2000 mm/year are lucky enough for collecting more rainfall. It is recommended to construct the roofs of the buildings in a way to enable rainwater harvesting.

The calculation of rainwater harvesting is considered to be a function of two parameters;

\[ \text{Annual precipitation amount} \times \text{surface area of the roof (m}^2) \]

It is important to note that there is not a month with none precipitation. That is an advantage in the sense of rainwater harvesting. Apart from the meteorological conditions, soil characteristics are also an important parameter in considering landscaping of the eco-city. Land levelling may be applied to collect and store rainwater as well as to construct water troughs, lagoons and wetlands for recreational use. As an example, Table 5 shows the long term average (1950-2015) monthly precipitation values of Istanbul.

**Water savings through collection of rainwater in the fictitious eco-city ABC located in Istanbul:**

When the roof area of an eco-building in Istanbul is assumed as 100 m\(^2\) regarding the long term average precipitation values

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>813.12</td>
<td>105</td>
<td>78</td>
<td>70.8</td>
<td>45.2</td>
<td>34.1</td>
<td>35</td>
<td>31.6</td>
<td>40.7</td>
<td>59.5</td>
<td>90</td>
<td>101.3</td>
<td>122</td>
</tr>
</tbody>
</table>

Annual ppt. = 813.12 mm (in other words; 813.12 litre of rainwater falls to each m\(^2\)). Thus, 813.12 litre x 100 m\(^2\) = 81 312 litre ~ 81 tons/year.

Taking into account the potential water losses due to unregulated precipitation regime, tank fullness, using different roof materials, escape of water from the roof, using different gutter systems, the water amount calculated is multiplied with a safety factor of 0.75 resulting in a much reliable water storage value of 81 x 0.75= 60.75 ~ 61 tons/year water may be stored.

Daily water consumption in Turkey is taken as 150 litre/capita. For example, for a family of 4 people monthly water consumption will be 18 m\(^3\) and water savings through rainwater collection from the roof with a surface area of 100 m\(^2\) will be equivalent to almost 3.38 months water need of the family residing in Istanbul. On the annual basis; 3.38/12 months= 0.28 years~28% of the annual water need may be supplied from rainwater. That is to say; almost 28% water saving may be possible on the yearly basis. In the planned eco-city ABC, the roof systems must be designed in a way to capture and collect rainwater as much as possible. Corresponding stage wise savings will be as follows;

- Stage 1= 232 000 m\(^2\) x 813 litre= 188 616 m\(^3\)/year x 0.75= ~ 388 m\(^3\)/day
- Stage 2= 188 000 m\(^2\) x 813 litre= 152 844 m\(^3\)/year x 0.75= ~ 314 m\(^3\)/day
- Stage 3= 90 000 m\(^2\) x 813 litre = 73 170 m\(^3\)/year x 0.75= ~ 150 m\(^3\)/day
- Stage 4= 188 000 m\(^2\) x 813 litre = 152 844 m\(^3\)/year x 0.75= ~ 314 m\(^3\)/day
- Total water saving via rainwater harvesting= 1166 m\(^3\)/day
Table 6 summarizes the overall daily water gain through greywater reuse and rainwater harvesting in a planned eco-city ABC settled in Istanbul.

![Table 6. Overall daily water gain in the fictitious eco-city ABC in Istanbul](image)

3. Results and Discussion

- Total population in the fictitious ABC eco-city = 100 000 people
- Daily water consumption = 100 000 x 150 litre/cap.day = 15 000 m$^3$/day
- Total Savings = 4 500 m$^3$/day via greywater + 1 166 m$^3$/day via rainwater = 5 666 m$^3$/day
- At least 38% of daily water demand may be provided from greywater and rainwater in the eco-city located in a region with a typical annual long term average rainfall of 813.12 mm. It is seen from this study that approximately 40% water gain is possible by greywater reuse and rainwater harvesting from the roofs.

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Retrofitting an Airport: Strategies to Reduce the Greenhouse Gas Emissions

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Keywords: Airport; retrofitting; carbon footprint; greenhouse gasses; sustainable development

Abstract

The objective of this study is to develop strategies to reduce greenhouse gas emissions of an international airport that will be retrofitted. For this purpose Sabiha Gokcen International Airport is evaluated in terms of its carbon footprint. The retrofitting of Sabiha Gokcen International Airport is assessed to elevate annual CO\textsubscript{2}e emissions from 540,545 tons to 1,208,300 tons. With measures taken to reduce the CO\textsubscript{2}e emissions, such as usage of electric cars for employee shuttles and airside vehicles, on-site recycling of used de-icer, construction of solar panels and metro services, it is possible to lower the greenhouse gas emissions by 21%.

1. Introduction

The aviation sector can be encountered as the most improved mode of transportation. In recent years, a drastic increase is observed in the number of people who preffered this fastest transportation track. Data presented by International Air Transport Association (IATA), shows 5.9% raise in revenue passenger kilometres (which is the product of number of passengers and the distance they travelled), in just one year (IATA, 2015). Besides within the next 15 years, the projections indicate an exponential growth will take place in airline revenue passenger kilometres on a global scale (Baxter et al., 2014). On the other hand, aviation industry generates negative environmental impacts such as greenhouse gas emissions that must be controlled and prevented (ATAG, 2015). Currently the aviation industry is responsible for 2% of all the anthropogenic carbon dioxide emissions (Monsalud et al., 2014). This percentage is expected to reach 15% by the year 2050 if necessary measures are not taken (Baxter et al., 2014; Whitelegg and Cambridge, 2004). According to the statistics of International Energy Agency (IEA), CO\textsubscript{2} emissions arising from international aviation bunkers shows an elevation of approximately 479% from 1990 to 2013 in Turkey (IEA/OECD, 2015) indicating the rapid growth of the sector. Flights together with the management of airports and their supporting infrastructure must be considered to develop sustainable aviation strategies.

In this context the objective of this study is to develop strategies to reduce greenhouse gas emissions of an international airport that will be retrofitted. Sabiha Gokcen International Airport, located on the Asian side of Istanbul, currently providing service to 23.6 million passengers annually, is examined in terms of its carbon footprint.
2. Materials and Methods

Similar to other civil airports, various companies are located within Sabiha Gokcen International Airport complex. This study is limited to the parts of the airport that are run by airport operator. Besides public and employee access to airport is also covered. By doing so a sound roadmap of practical importance towards reducing the greenhouse gas emissions can be put forward. The method adopted in this study is in accordance with operational control approach that defines the organizational boundaries (GHG, 2016).

Terminal building and common facilities are considered while calculating the greenhouse emissions. It should be noted that there is a tri-generator in the airport. However it is not possible to achieve the data related to the natural gas consumption of this tri-generator. Therefore this part is not included in the calculations.

Data gathered are fed to Airport Carbon and Emissions Reporting Tool (ACERT v3.1 calculation tool) (ACERT 2016) developed by Airports Council International (ACI) to get the greenhouse gas emissions (ACI, 2009). In this context source of emissions considered and the authority incharge is given in Table 1.

<table>
<thead>
<tr>
<th>Source of Emission</th>
<th>Authority Incharge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Airside vehicles</td>
<td>Airport Operator</td>
</tr>
<tr>
<td>Deicer usage</td>
<td>Airport Operator</td>
</tr>
<tr>
<td>Waste/wastewater processing</td>
<td>Airport Operator</td>
</tr>
<tr>
<td>Purchased electricity*</td>
<td>Airport Operator</td>
</tr>
<tr>
<td>Purchased natural gas**</td>
<td>Airport Operator</td>
</tr>
<tr>
<td>Aircrafts</td>
<td>Various Airline Companies</td>
</tr>
<tr>
<td>Access to Airport</td>
<td></td>
</tr>
<tr>
<td>Staff/visitor vehicles</td>
<td>Individual/Companies/Municipality</td>
</tr>
<tr>
<td>Employee vehicles</td>
<td>Individual/Companies/Municipality</td>
</tr>
<tr>
<td>Employee shuttles</td>
<td>Airport Operator</td>
</tr>
<tr>
<td>Cars/taxi</td>
<td>Individual/Companies/Municipality</td>
</tr>
<tr>
<td>Bus, hotel shuttle</td>
<td>Individual/Companies/Municipality</td>
</tr>
</tbody>
</table>

* Greenhouse gas emissions arising from the off-site generation of electricity (and heating or cooling) and purchased by the airport operator. Although there is a trigenerator operated in the airport, information on trigenerator can not be obtained.

** Greenhouse gas emissions arising from the off-site processing of natural gas and purchased by the airport operator.

3. Current Situation and Retrofitting

Sabiha Gokcen International Airport is located on the Asian side of Istanbul, about 50 kilometers away from the city centre (Taksim). It was started operating in 2001 for civil domestic and international flights. Currently Sabiha Gokcen Airport has one runway, four aprons, taxiways, a tower, an entrance control building, domestic and international terminal buildings, a cargo terminal, a hangar, a customs office building, a site for fuel, a wastewater treatment plant, a luggage handling and control system, a fire station, a police building, a regulator building, a
power centre, a heating and cooling plant and a solid waste collection and separation centre (Detam 2013). It provides service to 23.6 million passengers annually.

A new metro line that will connect Sabiha Gokcen to city will be opened in 2019. Besides in 2017, a 2nd runway will be in service (Detam 2013). Together with it two aprons, new taxiways, a new tower and a fire station will be opened. Due to the planned retrofitting, it is expected to have almost 71 million passengers using the airport annually. Besides there will be annually 556 830 flights (Detam 2013).

4. Results and Discussion

Unit water consumption (water consumption per passenger) is adopted as an indicator to evaluate the water usage in an airport. Various levels of water consumption ranging from 11 to 53 lt/passenger is stated in literature (Carvalho et. al., 2013; Couto et. al., 2015). The wide range indicates water conservation practices applied in an airport up to a level, as unit water consumption is also affected from factors such as the attitude of the people using the airport etc. 11 lt water consumption per passenger belongs to Atlanta Airport where water saving sanitary equipment and an air cooling system running without water cooling towers are used (Carvalho et. al., 2013). On the other hand, the highest figure of 53 lt/passenger is given for Narita Airport, although grey water collected from terminal restaurants are used for toilet flushing (Carvalho et. al., 2013). In Sabiha Gokcen International Airport, quite a low level of water namely, 17 lt is consumed per passenger as a result of reusing all the treated wastewater for landscape irrigation.

As a result of retrofitting CO₂ emissions are assessed to increase by a factor of 2.23, yielding 1,208,300 ton CO₂e per year. Figure 1 illustrates the contribution of various sources that are managed by airport operators, to CO₂e emissions after retrofitting.

As evident from Figure 1, de-icer usage has the highest share among others that contribute to greenhouse gas emissions. Similar to other Turkish airports, glycol is used as de-icer in Sabiha Gokcen International Airport. The usage of this deicer is calculated to generate 38,265 tons
CO\textsubscript{2}e. After de-icer usage electricity consumption comes. The third biggest contributor is the fuel usage of airside vehicles.

To lower the CO\textsubscript{2} e emissions generated by the activities performed by airport operators, the following measures can be taken (i.e. the authority in charge for all these measures will be the airport operator):

i. Usage of electric vehicles instead of fossil fuels such as diesel for operating both airside vehicles and employee shuttles.

ii. On-site recycling of used de-icer

iii. Establishing solar panels

As a result of applying all of these measures, the percent distributions given in Figure 2 are obtained.

![Diagram showing percent distribution of CO\textsubscript{2}e emissions](image)

**Figure 2.** Percent distribution CO\textsubscript{2} e emissions arising from activities performed by airport operators with measures taken after retrofitting

Due to shifting from cars using fossil fuels to electric cars the percentage of electricity consumption is increased. Fossil fuel usage for airside vehicles and employee shuttles results in generation of 22,380 tons CO\textsubscript{2}e. When electric cars and minibuses will be used for this purpose, it is possible to completely diminish CO\textsubscript{2}e emissions from this source. However, it must be noted that electric vehicle manufacturing results in more CO\textsubscript{2}e emissions than cars working with fossil fuels (Buekers et. al., 2014). On the other hand, lifetime CO\textsubscript{2}e emissions of electric cars are lower than the other cars (Buekers et. al., 2014).

The on-site recycling of deicer is evaluated to reduce the contribution of de-icer usage by 35\%, resulting in 13,400 tons CO\textsubscript{2}e emissions.

After retrofitting 28,385 ton CO\textsubscript{2}e will be released due to electricity consumption. In order to reduce this amount, it is recommended to construct solar panel systems. When 16,000 m\textsuperscript{2} area is covered with solar panels, it is possible to obtain 1,445 tonnes CO\textsubscript{2}e reduction.
Apart from all the mentioned measures access of people (passengers, employees, visitors etc.) to airport is an important source of CO₂ emissions. It is assessed that after retrofitting access to airport will generate annually 380,315 ton CO₂ emissions. This value represents staff / visitor / employee vehicles, busses etc. It is evaluated that with the establishment of the metro system, that will be opened in 2019, the mentioned CO₂ emissions will be decreased to 165,180 tons resulting in a 57 % reduction.

Figure 3 illustrates the share of CO₂ e emissions for Sabiha Gokcen International Airport according to the authorities in charge.

![Figure 3. Percent distribution of CO₂ e emissions with and without measures taken after retrofitting](image)

Airline companies are responsible for the highest portion of the CO₂ e emissions. After that comes ground access that is mainly controlled by the actions of municipalities. Than the smallest percentage is under the responsibility of the airport operator. The general picture for aviation sector depicts a similar profile. However the role of airport operators should not be underestimated as airports are inseparable parts of sustainable aviation systems.

The retrofitting of Sabiha Gokcen International Airport is evaluated to increase annual CO₂ emissions from 540,545 tons to 1,208,300 tons. However, with the recommendations mentioned (usage of electric cars for employee shuttles and airside vehicles, on-site recycling of used de-icer, construction of solar panels, metro services etc.) to reduce the CO₂ e emissions, it is possible to lower the greenhouse gas emissions by 21 %.

References


Evaluation of Printed Circuit Board Production through LCA Sensitivity Analysis

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

Abstract

The objective of this study is to bring to light the effects imposed by Cu recycling on environmental impacts of a printed circuit board (PCB) production facility with life cycle assessment (LCA). The data collected from an actual PCB manufacturing plant with a capacity of 22500 m\textsuperscript{2} PCBs/month is used for this purpose. Increasing the copper recycling from 30 \% to 47 \% in the etching step of PCB manufacturing is observed to yield benefits for all environmental impact categories. A substantial improvement of 44 \% decrease is obtained for ozone layer depletion potential (ODP). Besides 20 and 18 \% reductions are procured for freshwater aquatic ecotoxicity potential (FAEP) and marine aquatic ecotoxicity potential (MAEP), respectively.

1. Introduction

To visualize all the dimensions of environmental impacts arising from industrial facilities, a holistic approach is required. In this respect Life Cycle Assessment (LCA) provides a comprehensive perspective on environmental impacts. Such an approach gains importance especially when dealing with highly complicated industrial sectors where through many production processes, harmful impacts on both environment and human beings are obtained. Printed Circuit Board (PCB) production is a good example of the mentioned complicated manufacturing schemes. PCB is defined as a physical structure for mounting electronic components. In other words it is an important device for electrical interconnections between electronic components. All sorts of electronic equipments contain PCB’s. The main constituents of PCB’s are substrate, metals and adhesive for component attachment (Eshkeiti et al., 2015). In PCB production toxic metals, solvents, acids etc. are fed into (in some cases as much as 50) manufacturing steps (La Dou, 2006). Various auxiliary chemicals such as formaldehyde, lead, dimethylformamine, muriatic acid, copper sulfate, ethylene glycol, stannous chloride are involved in PCB manufacturing (La Dou, 2006; Hui et al., 2003). Some of these chemicals are hazardous in nature. LCA serves as a very valuable tool in evaluating the PCB production processes. There are research efforts that emphasize the importance of this tool in solving the problems related to the negative environmental impacts of PCB manufacturing (Liu et al., 2014). The results obtained will guide the manufacturers to develop strategies for the minimization of negative environmental impacts by addressing specific targets within the whole production scheme. For example a study on LCA of paper based PCB manufacturing shows the
advantages of paper based PCB over conventional organic based PCB. The results of LCA indicated that about two times lower magnitude impact can be obtained while producing paper based PCB (Liu et al., 2014).

In this context, the objective of this study is to evaluate the environmental impacts of different practices such as Cu recycling in a PCB production facility with LCA.

2. Material Methods

The investigated facility located in Turkey, manufactures PCB for white goods. The plant has a capacity of 22500 m$^2$ PCBs per month. Single layered and single sided boards (where circuits are printed onto only one side of the board) are processed to obtain PCBs for white goods. The board that is exported, is the main input to this production line. In other words the whole PCB production consists of a two consecutive stages, namely board/substrate fabrication followed by the manufacturing of PCB. Intensive data is gathered from the actual facility that manufactures PCB for about 6 months. Although not realized in the factory under investigation the board production is also included in the LCA model by adopting literature data. As a result the application of Cu recycling during the PCB manufacturing makes sense as Cu is actually an ingredient of board itself. The LCA model consider both board fabrication and PCB manufacturing. However both the use and end of life (EoL) phase of the PCB are not covered. The study is valid until there is change in the production line. Ecoinvent integrated GaBi software is used for the LCA model and CML 2001 (Guinée et. al., 2001) method is used to calculate the results in terms of global warming potential (GWP), acidification potential (AP), marine aquatic ecotoxicity potential (MAEP), freshwater aquatic ecotoxicity potential (FAEP), ozone layer depletion potential (ODP), terrestrial 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 results are given per 1 m$^2$ ready-to-use PCB. The flowchart of whole PCB manufacturing process is illustrated in Figure 1.

Figure 1. Whole PCB production processes

The technical properties of the product is tabulated in Table 1.
Table 1. Technical properties of the product

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Epoxy resin, glass fiber, copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biodegradability</td>
<td>Nondegradable</td>
</tr>
<tr>
<td>Flammability standard</td>
<td>UL-V0</td>
</tr>
<tr>
<td>Flame resistance (sec)</td>
<td>30-35</td>
</tr>
<tr>
<td>Moisture resistance</td>
<td>Good</td>
</tr>
<tr>
<td>Layer/ Side</td>
<td>Single layer/single sided</td>
</tr>
<tr>
<td>Flexural strength (Crosswise, Lengthwise) (kg/m²)</td>
<td>31.10 – 32.00, 39.80 – 40.70</td>
</tr>
<tr>
<td>Solder mask</td>
<td>Epoxy resin (Green)</td>
</tr>
<tr>
<td>Thickness of PCB (mm)</td>
<td>1.65</td>
</tr>
<tr>
<td>Thickness of solder mask (µm)</td>
<td>20-25</td>
</tr>
<tr>
<td>Thickness of copper (µm)</td>
<td>35</td>
</tr>
<tr>
<td>Dielectric constant (GHz)</td>
<td>4.650 – 4.700</td>
</tr>
<tr>
<td>Dielectric loss factor (GHz)</td>
<td>0.013 – 0.015</td>
</tr>
</tbody>
</table>

Production steps of PCB manufacturing can be summarized as: Boards are cut with a saw in the cutting stage. After cutting, circuit printing comes. A rinsing step is then applied to remove dust from the surface of the board. After drying, a silk screen is used to print the circuit with an etching resist ink onto copper surface of the board. The circuit printed board is dried in an UV furnace. Cleaning solvents and fabrics are used to clean up the squeegee used during silk screen printing. In the subsequent etching process all copper surfaces except circuit ways which are protected by etching resist ink, are removed. Hydrochloric acid is used to dissolve copper from the surface of the board. In this process, 30% of the dissolved copper is collected for recycling. After etching, etching resist ink is removed from the surface with NaOH and the board is rinsed. Generated wastewater is directed towards wastewater treatment plant. In the solder mask stage, to protect the substrate from corrosion and electrical shorts, surface of the circuit board without copper is coated with an epoxy based solder mask, and dried in UV furnaces. Similar to circuit printing step, cleaning solvents and fabrics are used to clean up squeegee used during solder mask application. In the legend printing process, epoxy based dye is used to print and denote the locations, names and codes of electronic components which will be placed onto PCB. Legend printing process is applied for both back and front sides of the PCB. PCB is then dried in UV furnaces. Cleaning solvents and fabrics are used also in legend printing process. Protective coating is applied to prevent oxidation of copper circuit ways. Surface of the boards are coated with lead free solder in HASL (Hot Air Solder Line) machine to obtain a flat and smooth surface. After coating, excess solder on the surface is removed by applying air jets. PCBs are drilled for placement of electronic components on the board. As final finishing, PCBs are cleaned up with water. Testing is performed to control the possible unwanted open and short circuits. During all operations deionised water is used for rinsing or cleaning. Usage of wetting oil in protective coating process is not covered as no information about this specific chemical is found in databases and literature. Besides, VOC emissions are not included in the study due to the absence of them in the database. Textile, plastic and metal wastes are collected in one place throughout the manufacturing of PCB process. Waste plastic thinner and alcohol containers are distributed among various parts of the processes by considering the amount of
thinner and alcohol usage per m² PCB. Similarly, waste tin paint cans are allocated between processes based on the amount of paint used per m² PCB. The total amount of textile wastes is equally divided among related processes in the model. Textile waste includes all oily rags and waste personnel protective equipment. Dusts arising from cutting stage and textile wastes are considered as hazardous wastes. Aggregated inventory data is outlined in Table 2.

Table 2. Aggregated inventory data

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Material</th>
<th>Amount</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fabrication of Board</td>
<td>Glass fiber woven</td>
<td>0.610</td>
<td>kg/m²</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>1.596</td>
<td>kg/m²</td>
</tr>
<tr>
<td></td>
<td>Epoxy resin</td>
<td>1.600</td>
<td>kg/m²</td>
</tr>
<tr>
<td></td>
<td>Water (fabrication)</td>
<td>0.407</td>
<td>m³/m²</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manufacturing of PCB</td>
<td>Water*</td>
<td>0.058</td>
<td>m³/m²</td>
</tr>
<tr>
<td></td>
<td>Water**</td>
<td>0.054</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Solvents</td>
<td>0.069</td>
<td>kg/m²</td>
</tr>
<tr>
<td></td>
<td>Etchant*</td>
<td>1.89</td>
<td>kg/m²</td>
</tr>
<tr>
<td></td>
<td>Etchant**</td>
<td>0.611</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Etching resist ink</td>
<td>0.011</td>
<td>kg/m²</td>
</tr>
<tr>
<td></td>
<td>NaOH</td>
<td>0.008</td>
<td>kg/m²</td>
</tr>
<tr>
<td></td>
<td>Solder mask</td>
<td>0.051</td>
<td>kg/m²</td>
</tr>
<tr>
<td></td>
<td>Solder bar</td>
<td>0.004</td>
<td>kg/m²</td>
</tr>
<tr>
<td></td>
<td>Flux</td>
<td>0.014</td>
<td>L/m²</td>
</tr>
<tr>
<td></td>
<td>Energy</td>
<td>7.135</td>
<td>kWh/m²</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Outputs</th>
<th>Material</th>
<th>Amount</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product</td>
<td>PCB</td>
<td>1</td>
<td>m²</td>
</tr>
<tr>
<td>Waste</td>
<td>Textile waste (contaminated)</td>
<td>0.019</td>
<td>kg/m²</td>
</tr>
<tr>
<td></td>
<td>Plastic waste (contaminated)</td>
<td>0.004</td>
<td>kg/m²</td>
</tr>
<tr>
<td></td>
<td>Metal waste (contaminated)</td>
<td>0.009</td>
<td>kg/m²</td>
</tr>
<tr>
<td></td>
<td>Board waste (hazardous and non-hazardous)</td>
<td>0.094</td>
<td>kg/m²</td>
</tr>
<tr>
<td></td>
<td>Wastewater*</td>
<td>0.465</td>
<td>m³/m²</td>
</tr>
<tr>
<td></td>
<td>Wastewater**</td>
<td>0.461</td>
<td>m³/m²</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>0.27</td>
<td>kg/m²</td>
</tr>
<tr>
<td></td>
<td>Copper*</td>
<td>0.091</td>
<td>kg/m²</td>
</tr>
<tr>
<td></td>
<td>Copper** (recovered in the factory)</td>
<td>0.1295</td>
<td>kg/m²</td>
</tr>
<tr>
<td></td>
<td>Solder slag</td>
<td>0.003</td>
<td>kg/m²</td>
</tr>
<tr>
<td>Emissions</td>
<td>TOC (Propane)</td>
<td>2.83×10⁻³</td>
<td>kg/m²</td>
</tr>
<tr>
<td></td>
<td>Dust</td>
<td>4.9×10⁻⁵</td>
<td>kg/m²</td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>5.47×10⁻⁶</td>
<td>kg/m²</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>5.47×10⁻⁶</td>
<td>kg/m²</td>
</tr>
</tbody>
</table>

*: 30% Cu recycling  **: 47% Cu recycling

As indicated earlier in the etching process all copper surfaces except circuit ways are removed. As an etching agent hydrochloric acid is used. In this process only 30 % of the dissolved copper is recovered for recycling. This level of copper recycling represents the base scenario. With the help of improving the equipment it is possible to elevate the copper recycle up to 47 %. This study examines the effects of such an improvement on environmental impacts. Table 3 presents the parameters related to base scenario (with 30 % Cu recycle:A) and improvements made (with 47 % Cu recycle:B) in etching operations. It must be noted that all the data used in modelling are obtained from the actual plant.

Table 3. Data related to various levels of Cu recycling in etching operations

<table>
<thead>
<tr>
<th>Parameters</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu recycle (%)</td>
<td>30</td>
<td>47</td>
</tr>
<tr>
<td>Recovered Cu (kg/m²)</td>
<td>0.0910</td>
<td>0.1295</td>
</tr>
<tr>
<td>Consumed Etchant (kg/m²)</td>
<td>1.890</td>
<td>0.611</td>
</tr>
<tr>
<td>Consumed Water (m³/m²)</td>
<td>0.00630</td>
<td>0.00203</td>
</tr>
<tr>
<td>Disposed Cu (kg/m²)</td>
<td>0.18</td>
<td>0.14</td>
</tr>
</tbody>
</table>
3. Results and Discussion

The results of the modelling study is presented in Table 4.

Table 4. Effect of Cu recycling on environmental impacts of the whole PCB production A: 30 % Cu recycling; B: 47 % Cu recycling

<table>
<thead>
<tr>
<th>Impact Category</th>
<th>Unit</th>
<th>A</th>
<th>B</th>
<th>% Reduction Obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>GWP</td>
<td>kg CO₂ eq</td>
<td>23.1</td>
<td>21.9</td>
<td>5</td>
</tr>
<tr>
<td>AP</td>
<td>kg SO₂ eq</td>
<td>0.135</td>
<td>0.13</td>
<td>6</td>
</tr>
<tr>
<td>MAEP</td>
<td>kg DCB eq</td>
<td>7.44×10^4</td>
<td>6.12×10^4</td>
<td>18</td>
</tr>
<tr>
<td>FAEP</td>
<td>kg DCB eq</td>
<td>2.35×10^3</td>
<td>1.88×10^3</td>
<td>20</td>
</tr>
<tr>
<td>ODP</td>
<td>kg R11 eq</td>
<td>2.50×10^6</td>
<td>1.39×10^6</td>
<td>44</td>
</tr>
<tr>
<td>TETP</td>
<td>kg DCB eq</td>
<td>0.276</td>
<td>0.241</td>
<td>12</td>
</tr>
<tr>
<td>POCP</td>
<td>kg Ethene eq</td>
<td>1.17×10^-2</td>
<td>1.10×10^-2</td>
<td>4</td>
</tr>
<tr>
<td>ADP Fossil</td>
<td>MJ</td>
<td>2.65×10^2</td>
<td>2.48×10^2</td>
<td>5</td>
</tr>
<tr>
<td>ADP Elements</td>
<td>kg SB eq</td>
<td>1.16×10^-3</td>
<td>1.16×10^-3</td>
<td>8</td>
</tr>
<tr>
<td>EP</td>
<td>kg Phosphate eq</td>
<td>0.191</td>
<td>0.18</td>
<td>4</td>
</tr>
<tr>
<td>HTP</td>
<td>kg DCB eq</td>
<td>39.7</td>
<td>36.8</td>
<td>7</td>
</tr>
</tbody>
</table>

As can be seen from Table 3, even elevating copper recycling from 30 % to 47 % in the etching step of PCB manufacturing yields benefits for all environmental impact categories. A substantical improvement of 44 % reduction is obtained in ODP. Apart from this finding it is found that FAEP and MAEP can be lowered by 20 and 18 %, respectively with the application of the mentioned improvement.

Acknowledgements

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References

Towards a Greener Port: Reducing the Carbon Footprint

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Keywords: Port; carbon footprint; greenhouse gasses; sustainable development

Abstract

This study deals with the greenhouse gas emissions arising from a port located in the most industrialized region of Turkey. In the port under investigation liquid load, dry load, cargo and container loading and unloading processes take place. To lower the carbon footprint, light-emitting diodes (LEDs) are installed for illumination and the cargo handling equipments using fossil fuels are replaced with the ones working with electricity. By adopting the mentioned strategies to reduce the carbon footprint of the facility, 14\% reduction in greenhouse gas emissions is realized.

1. Introduction

Due to its financial benefits maritime transport of cargo is the most preferred mode of conveyance (Velásquez and Martínez de Osés, 2013). While targeting an environmentally sustainable maritime transportation system, together with ships, ports and their supporting infrastructure must be considered (Cusano Inés, 2013). In this respect appraisal of environmental impacts of port areas is an important issue and a lot of research effort is dedicated to convert these facilities into more environmentally friendly ones (Lam and Notteboom, 2014; Chiu et. al., 2014; Beskovnik and Bajec, 2015; Lirn et. al., 2013; Anastasopoulos et. al., 2011; Pavlic et. al., 2014; Tommasetti et. al., 2014; Chang and Wang, 2012).

Currently the shipping sector is responsible for 2.4\% of all the anthropogenic carbon dioxide emissions and this share is expected to elevate in the future as indicated by International Maritime Organization (IMO) (Winnes et al., 2015). Although maritime transport is stated to generate relatively low greenhouse gas emission levels when compared with other transportation options (Velásquez and Martínez de Osés, 2013), a lot of ports located all around the world are calculating their carbon footprint to develop strategies for reducing greenhouse gas emissions arising from them (Villalba and Gemechu, 2011; SRI and SC&A, 2014; Shin and Cheong, 2011). The European Sea Ports Organization (ESPO) recommends investigating CO\textsubscript{2} footprint for ports and then constructing necessary precautions to lower greenhouse emissions based on these findings (Carballo-Penela et. al., 2012). Besides ESPO promotes all sorts of measures that will cause 20\% reduction of carbon footprint by the year 2020 (Carballo-Penela et. al., 2012).

Being a country surrounded by the sea on three sides, Turkey holds the 13th place in world container port traffic volume (Canbulat et. al., 2015). A rapid rise is observed in handled containers (Canbulat et. al., 2015). In this context the main objective of this study is to investigate the carbon footprint of a Turkish port where liquid load, dry load, cargo and
container loading and unloading operations are performed. The effect of ameliorates made to reduce the greenhouse gas emissions are emphasized.

2. Material Methods

The investigations on greenhouse gas emissions of the port are mainly performed by using Guidelines for National Greenhouse Gas Inventories developed by Intergovernmental Panel on Climate Change (IPCC, 2006). Calculation methodology and the emission factors are adopted from the mentioned guidelines. Due to difficulties faced during data collection, Tier 1 (general default) and Tier 2 (country specific) approaches are taken into account for calculating the greenhouse emissions. Calculation of cumulated uncertainty on the other hand is conducted by using Greenhouse Gas (GHG) Protocol, developed by World Resources Institute (WRI) and World Business Council on Sustainable Development (WBCSD) (GHG, 2016).

3. Location and Utilities

The port under investigation is located in İzmit which is the most densely industrialized region in Turkey. It is 16 and 15 km away from railwas and highway respectively (Bal, 2015). Loading and unloading operations are perfomed continuously on a 24 hour basis and currently 91 workers are employed. The port has started giving service in 1992. Annual handling capacity of the port can be summarized as: 1,150,000 ton of general cargo plus 250,000 TEU (The twenty-foot equivalent unit is an unit of cargo capacity) of container plus 1,000,000 ton of bulk liquid load and 120,000 ton of bulk dry load (Bal, 2015). The port has a storage tank capacity of 124,000 m³ and an outdoor storage area of 38,516 m² (Bal, 2015). There exists two piers in the port. Annually 500 ships can dock the first pier that has a length of 165 meters. The second pier has an annual capacity of 400 ships and has a length of 240 meters. The equipments used in the port are tabulated in Table 1.

<table>
<thead>
<tr>
<th>Type of Equipment</th>
<th>Handling</th>
<th>Handling Equipment</th>
<th>Capacity (ton)</th>
<th>Number of Equipment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Road Vehicles</td>
<td>Terminal tractor</td>
<td>50</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Other Equipment</td>
<td>Mobile crane with rubber wheels (tires)</td>
<td>150</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Crane with palette</td>
<td>7</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Container reach stacker (CRS)</td>
<td>45</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Empty container reach stacker (ECS)</td>
<td>4</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Forklift</td>
<td>3 5 25</td>
<td>1 1 1</td>
<td></td>
</tr>
</tbody>
</table>

In port areas two type of main processes take place, namely unloading and loading processes. Simplified flowchart of loading process is illustrated in Figure 1. The dry load/cargo/container
of the berthed ship is first unloaded by the cranes. Then the goods are either stacked within the port area or directly loaded to vehicles for dispatching.

![Diagram](image.png)

**Figure 1.** Dry load/cargo/container unloading processes

As given in Figure 2, the goods (in the form of dry load/cargo/container) that will be transported by the ship are either stacked in the port area or directly loaded to the vessel.

![Diagram](image.png)

**Figure 2.** Dry load/cargo/container loading processes

### 4. Results and Discussion

As given in Table 2, the CO₂e emissions generated in the port is calculated as 861,121 tons for the year 2015. 43% of the CO₂e emissions are observed to arise from direct sources.
In order to reduce the greenhouse gas emissions in 2014, light-emitting diodes (LEDs) are installed for illumination. In 2015, cargo handling equipments using fossil fuels are replaced with the ones working with electricity.

The effect of the mentioned amelioration on the level of greenhouse gas emissions are summarized in Table 3.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cargo Handling Equipment</td>
<td>729,867</td>
<td>350,154</td>
<td>52 % decrease</td>
</tr>
<tr>
<td>Electricity Usage</td>
<td>251,515</td>
<td>490,372</td>
<td>95 % increase</td>
</tr>
<tr>
<td>Total</td>
<td>981,382</td>
<td>840,526</td>
<td>14 % decrease</td>
</tr>
</tbody>
</table>

As given in this table, although the electricity input is increased by 95 % with the measures taken, usage of light-emitting diodes (LEDs) instead of other types of bulbs and cargo handling equipments working with electricity is observed to decrease overall greenhouse gas emissions by 14 %.

Assessed emissions has 6.1 % cumulated uncertainty that can be ranked as "good".
References


Reactivation of Waste Automobile Catalytic Converters for the Water Treatment Purposes

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\textsuperscript{b} Department of Environmental Engineering, University of Kocaeli, Kocaeli, Turkey.

Keywords: Automobile Catalytic Converter, Reactivation, Regeneration, Reuse, Spent Catalyst.

Abstract

The spent catalysts are valuable wastes that need to be completely destructed and treated, because they are the potential resource of Platinum Group Metals (PGMs). Reuse and recycling of PGMs are limited because of the complexity of the applied techniques and their disadvantages. In this study we aimed the reuse of waste catalytic converter in a new area and more applicable way. For this purpose, Powdered Waste Catalytic Converter form (PWCC; waste catalytic converter; crushed, milled, washed with pure water and dried) used as a catalyst in a Catalytic Wet Air Oxidation (CWAO) reaction to degrade a model pesticide aqueous solution (malathion). And also we tried to reactivate PWCC, for better pesticide removal efficiency. As well as different activation methods and also the combination of activation techniques applied to PWCC, which are more practical and environmental friendly.

1. Introduction

Platinum Group Metals (PGMs) such as platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), iridium (Ir) etc. are widely used in many industrial processes linked to their properties such as catalytic activity, chemical stability, corrosion resistance and magnificent color (Dong et al. 2015). Automobile catalytic converters are the main usage area of PGMs, with the proportion more than 50% of PGMs’ market (Nogueira et al. 2014). Pt and Pt/Rh were firstly used in primary autocatalytic converters then Pd/Rh mixtures were introduced to car exhaust systems after the usage of unleaded fuel (Heck and Farrauto 2001). In a catalytic converter, the catalyst (in the form of platinum and palladium) is coated onto a ceramic honeycomb or ceramic beads that are housed in a muffler-like package attached to the exhaust pipe. The catalyst helps to convert carbon monoxide into carbon dioxide. It converts the hydrocarbons into carbon dioxide and water. It also converts the nitrogen oxides back into nitrogen and oxygen. Figure 1 shows the structure of the automobile catalytic converter.

When a catalytic converter got lost its performance and not meets the required emissions standards, it has to be changed by a new one. Spent catalytic converters are valuable waste that need to be completely destructed and treated, because it is a potential resource of PGMs (Christou et al. 2007). On the other hand when we evaluate this group of waste from the point of environmental protection, its known that spent catalysts are harmful to the environment due to the presence of soluble/leachable organic and inorganic compounds (Reddy et al. 2010).
And also PGMs existence in the secondary sources (in spent catalyst materials) at high concentration levels when compared to the primary sources, makes the recovery, regeneration and reuse of this waste feasible (Suoranta et al. 2015). PGMs can be recovered from spent catalyst materials using pyro-metallurgical and hydrometallurgical methods. In pyrometallurgical method, PGMs are concentrated in the metal phase or converted to easily processed compounds and then, refinerization processes is applied to recover PGMs. In hydrometallurgical method PGMs are recovered by dissolving in acids or acid mixtures like aqua-regia, in the presence of oxygen, bromine, iodine, chlorine, hydrogen peroxide, etc. (Dong et al. 2015). But these techniques have many disadvantages like complexity, producing byproducts that toxic and the persistent on the environment and also being highly energy consuming etc. According to report that published in 2011, the global sales of Pt; Pd; Rh were 245; 299; 27.2 tons, respectively. About 46% of the total Pt, 57% of the Pd and 77% of the Rh were used by automotive catalyst industry and the same year only about 23% of the Pt and Pd, 25% of Rh recovered from the recycling (USGS, 2011). These lower reuse and recycling levels show that a new approach is mandatory.

Another usage area of PGMs is environmental protection systems. In the water treatment processes, platinum and palladium largely used as a heterogeneous catalyst to treat wastewater or to convert non-biodegradable forms to biodegradable forms. In this study PWCC was treated with different methods for regeneration and reactivation of PGMs to catalyze Catalytic Wet Air Oxidation (CWAO).

2. Material Methods

2.1. Catalyst treatment
The waste catalytic converters used in the study were taken from a local car maintenance service. After cutting off the external metal parts of the catalytic converters only a monolithic substrates are washed with tap water several times and dried. Then, they crushed with the jaws crusher until it became less than 250-400 meshes (Figure 2).

Than chosen techniques applied to PWCC. Summary of the reactivation processes are given in Figure 3. For all reactivation experiments experiments 5gr. PWCC was used.

2.2. X-Ray Fluorescence Spectrometry
PWCC was characterized with X-Ray Fluorescence Spectrometry (XRF) to determine metal content of the material. For XRF analyses, samples were dried overnight at 65°C, dried at 105°C for two hours and prepared as pellets by covering pellets (made with boric acid). Rigaku ZSX Primus II was used for XRF analyses.
2.3. Catalytic Wet Air Oxidation Procedure
The batch reactions were performed in a hastelloy 0.6 L batch reactor equipped with a magnetic stirrer, digitally controlled oil circulated heating jacket, sampling system and the monometer. Reactor was supplied from Bushi Glassuster, Switzerland. In the standard procedure of catalytic wet oxidation 400 ml of sample solution and the required quantity of PWCC was put in to the reactor. The reactor was safely closed and the reaction was set to the desired level. Then, the reactor was filled with dry air allowing to control the reaction pressure value. The circulator was opened and this point was the beginning of the reaction in all experiments. All samples were filtered by 0.45µm filter paper and analyze as soon as possible with HPLC-UV.

2.4. HPLC Analysis
Initial and residue concentration of malathion after CWAO were measured by an Agilent 1260 Infinity HPLC with a UV detector. A 250 mm long C-18 capillary column (Eclipse XDB, Agilent) with an internal diameter of 4.6 mm was used to separate compounds. A 50:50 v/v mixture of ultra pure water: acetonitrile was used as a mobile phase. Flow rate was set to 1 mL/min.

3. Results and Discussion
According to XRF analyses metal content of the PWCC is given in Table 1. Ce and Pd, which have the main catalytic effect on the oxidation reactions, detected in the PWCC (before regeneration processes) in the percentage of 7.12% and 1.07% respectively.

Table 1. Metal content of the PWCC

<table>
<thead>
<tr>
<th>No</th>
<th>Component</th>
<th>% wt</th>
<th>No</th>
<th>Component</th>
<th>% wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Al</td>
<td>30</td>
<td>10</td>
<td>Nd</td>
<td>1.14</td>
</tr>
<tr>
<td>2</td>
<td>Si</td>
<td>26</td>
<td>11</td>
<td>Pd</td>
<td>1.07</td>
</tr>
<tr>
<td>3</td>
<td>Zr</td>
<td>14.5</td>
<td>12</td>
<td>Ti</td>
<td>0.785</td>
</tr>
<tr>
<td>4</td>
<td>Mg</td>
<td>7.85</td>
<td>13</td>
<td>K</td>
<td>0.585</td>
</tr>
<tr>
<td>5</td>
<td>Ce</td>
<td>7.12</td>
<td>14</td>
<td>S</td>
<td>0.436</td>
</tr>
<tr>
<td>6</td>
<td>Sr</td>
<td>3.33</td>
<td>15</td>
<td>Ca</td>
<td>0.373</td>
</tr>
<tr>
<td>7</td>
<td>Ba</td>
<td>2.30</td>
<td>16</td>
<td>P</td>
<td>0.353</td>
</tr>
<tr>
<td>8</td>
<td>La</td>
<td>2.02</td>
<td>17</td>
<td>Hf</td>
<td>0.314</td>
</tr>
<tr>
<td>9</td>
<td>Fe</td>
<td>1.49</td>
<td>18</td>
<td>Zn</td>
<td>0.106</td>
</tr>
</tbody>
</table>
Obtained removal efficiencies in wet oxidation of malathion with reactivated catalysts are given in Figure 4. When Figure 4 analyzed it is seen that PWCC5* gives the best result for the CWAO of malathion. PWCC5* was prepared by the reactivation process included, n-hexane extraction and thermal elimination of organic impurities. This application developed the PWCC performance from 29% to 33% (PWCC5). And application of additional thermal reduction to the PWCC5, in the flow of H₂ at 400°C caused the better catalytic activity and the removal efficiency reached to level of 38% (PWCC5*).

![Figure 4: Pesticide removal efficiency of reactivated catalysts at CWAO processes (malathion concentration 20 ppm, at 30 bar pressure, 60°C reaction temperature, added catalyst 0.5 gr, reaction time 2 hours, for all processes.)](image)

As a result, this study shows that using waste automobile catalytic converter in the catalytic processes is a valuable suggestion. With this perspective development of the this material’s catalytic activity in advanced oxidation processes and practicing it in new catalytic processes will interest the researchers who works about recycling and reuse and advanced water treatment technologies.
Figure 3. Applied reactivation techniques to PWCC
References


Life Cycle Assessment of Cotton Home Textile Products

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Keywords: Bed-sheets, cotton, environmental impacts, life cycle assessment, SimaPro, textile industry.

Abstract

Although textile products take place in every area of our lives and the very large proportions of consumption, studies in recycling textile is not as it should be. Life Cycle Assessment (LCA), starting from obtaining raw materials which are used in manufacturing a product or service, including all related production, shipping, consumer use and post-use as waste disposal, the life cycle, a method, is used to determine the environmental impact at different stages for reporting and managing. This method, which was standardized by ISO 14040:2006 and ISO 14044:2006 is a decision support tool for evaluation of environmental impacts of products and services, required for a particular. The objective of the present study was to examine and compare the environmental impacts of cotton textile products by means of LCA. The comparative LCA was performed using LCA software SimaPro® with CML-IA baseline method. This study shows that LCA which can provide a useful comparison among products and is helpful in decision making.

1. Introduction

Cotton textile industry is a very complex and one of the world’s largest industries (Resta ve Dotti, 2015). Textile production has a complex structure and different material types, thereby fibre production methodologies and yarn spinning processes can be used for various product types. The textile manufacturing process consumes resources such as water, fuel and different types of chemicals along its life cycle and generates a significant amount of waste which causes a number of different environmental problems such as pollution of air, land and water throughout the releases of toxic and hazardous waste (Eryurek, 2015). Textile industry is one of the significant contributors to the Turkish economy constituting 18% of total export volume in 2013 according to Turkish Statistical Institute (Baydar et al., 2015).

Life Cycle Assessment (LCA) is a method to measure total environmental effects of a product “from cradle to grave” (Eryurek, 2015). Several studies have been carried on different textile categories, including medical textiles (Ponder, 2009), bed sheets (De Daxce et al., 2012), bathrobe (Güngör et al., 2009), T-shirts (Baydar et al., 2015; Zhang et al., 2015), etc., most of which are 100% cotton or 50% cotton/50% polyester. This method can be used to quantify the environmental impacts of materials, processes, products or systems during their entire lifetime from creation to disposal. This methodology, which was standardized by ISO 14040 series is a decision support tool for evaluation of environmental impacts of products and services, required for a particular (Baydar et al., 2015). The LCA process can be divided into four phases according to ISO 14001; Goal and Scope Definition, Life Cycle Inventory Analysis (LCI), Life Cycle Impact Assessment (LCIA) and Interpretation (Fig. 1) (ISO 14040, 2006; Polat and Bektas, 2015).
The objective of the present study was to examine and compare the environmental impacts of 100% cotton bed-sheets by means of LCA in Turkey. The comparative LCA was performed using LCA software SimaPro® with CML-IA method.

2. Material Methods

In this step, the necessary data for LCA study was collected to quantify the inputs and outputs of the processes. The LCA software program calculated the inputs and outputs of bed-sheet manufacturing process using process simulation. Information for raw material and energy inputs uses in the bed-sheets manufacturing was collected from the mill itself.

100% cotton dyed bed-sheets is choosen as the declared unit. The functional unit selected was one kilogram cotton production.

The system boundary of bed-sheets is shown in Fig. 2, which takes into account two major phases of the dyed cotton bed-sheet’s life cycle.

3. Results and Discussion

The environmental effects of the 100% cotton single dyed sheets are given as a diagram on Fig 3. As it is seen on the diagram that the greatest impact on the production phase of the sheet is caused during the dyes and finishing processes since vinyl sulfonyl group of dyes are used in the dyeing process. This diagram shows that since the item is a textile product has more environmental impact in the stage of use than in the stage of production.
According to the specified impact categories, washing stage is in the first place except for the "ozone layer depletion" and "human health toxicity" categories. The reason that the production stage is effective on depletion of the ozone layer categories is the emission value which is caused by during the dye finishing and sizing process.

In all impact categories, it has been determined that fabric-finishing process has much more affect than the dyeing process.

**Figure 2.** System boundary and processes for the cotton bed-sheets
To see the net impact of the dyeing process, a comparison of the impact categories of the SimaPro modelled 100 % cotton single white bed-sheets with CML-IA baseline method on a 100 % cotton single sheet’s dyeing process is given on Fig. 4.
Results from the software underline the estimated environmental performance of cotton textile production in terms of a number of choices such as carbon footprint, resource and energy consumptions and various environmental impacts.

Conclusions
In this study, from the production process of, cotton home textile products of 100% cotton single dyed bed-sheets to the final process of user’s end waste product’s inventory analysis, waste scenarios and impact assessment process are performed in a computer software called the SimaPro 8.0.4 by selecting the baseline method CML-IA. It was determined that product indicated the biggest environmental impact in the consumption phase of the life cycle.

This study show that LCA which can provide a useful comparison among products and is helpful in decision making.

Acknowledgments
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References
**Required Ozone Doses For Removing Natural Estrogenic Hormones From Wastewater Effluents**

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**Keywords:** Estrogenic hormones, 17β-estradiol, Estrone, endocrine disrupting hormones

**Abstract**

Wastewater treatment plant (WWTP) effluents contain a mixture of estrogens. 17β-estradiol and estrone are most found in WWTP effluents and consequently surface waters. These hormones has known endocrine disrupting effects in the aquatic environment, thus, it is a contaminant of emerging concern.

In this study, by the aim of removal of endocrine disrupting hormones in a treatment plant effluent, 17β-estradiol and estrone concentrations determined and required ozone doses was investigated. Ozonation in effluent of treatment plant studies showed that, 17β-estradiol and estrone was removed with 14 mg/l ozone dosage in 2 minutes by the efficiencies 96% and 95%, respectively.  

1. **Introduction**

Estrogenic hormones have an adverse impact on public health and wildlife (Hamid and Eskicioğlu, 2012; Tyler et al., 2005). Increased levels of estrogenic hormones are believed to be associated with cancers of the reproductive system (Samavat and Kurzer, 2015; Knowlton and Lee, 2012; Corey et al., 2002; Pandini et al., 2007). With the recent widespread concerns of the environmental and public health effects of endocrine disrupting hormones, it is becoming important to develop new techniques to remove these substances from wastewater, such as ozonation, advanced oxidation processes, activated carbon, and membrane technology (Li et al., 2016).

One of the most effective removal of endocrine disrupting chemical (EDC) is ozonation; However removal efficiency depend on structure of pollutant and amount of ozone doses (Zwiener et al., 2000).

Bila et al. (2007) investigated in their study, degradation of 17β-estradiol using ozone, at 3 different pH (3, 7 and 11). At pH 7 and pH 11 could be eliminate all of the 17β-estradiol concentration in the wastewater. The by-products after ozonation were at least in pH 7 determined (Bila et al., 2007).

2. **Material Methods**

Wastewater samples were taken from Ataköy Wastewater Treatment Plant (WWTP) effluent and bottled in opaque brown glass sampling bottles and were stored at +4 °C according to storage conditions determined in Standard Methods.
17β-estradiol and estrone hormone solutions were prepared from Cayman commercial brand stock solutions. First they were weighted, then dissolved in methanol and diluted with 1% methanol–distilled water.

DRG-Diagnostics brand 17β-estradiol kit and DiaMetra brand estrone kit were used for reading the values in Perlong DNM-9602 model enzyme linked immunoassay (ELISA) reader set.

Degremont / Triogen model ozone generator, 4 g / hr flow rate capacity, was used in the ozonation experiments. Stainless steel reactor is 5 L volume and allows the wastewater to be circulated in the reactor using a pressure pump. The process was operated in a semi-batch mode (APHA, AWWA – WEF, 2005).

![Ozonation Process](image)

**Figure 1. Ozonation Process**

### 3. Results and Discussion

Hormone concentrations in WWTP effluent samples was measured at the time and ozone consumption was calculated (Table 3.).

<table>
<thead>
<tr>
<th>Time (minute)</th>
<th>Concentration (ng/L)</th>
<th>Removal efficiency (%)</th>
<th>Ozone requirement (mg/L)</th>
<th>Concentration (ng/L)</th>
<th>Removal efficiency (%)</th>
<th>Ozone requirement (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>17β-estradiol</td>
<td></td>
<td></td>
<td>Estrone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>240</td>
<td>0</td>
<td>0</td>
<td>171</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>61</td>
<td>75</td>
<td>9</td>
<td>46</td>
<td>73</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>9.6</td>
<td>96</td>
<td>14</td>
<td>8.5</td>
<td>95</td>
<td>14</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>99</td>
<td>16</td>
<td>1.4</td>
<td>99</td>
<td>17</td>
</tr>
</tbody>
</table>
Removal efficiency of 17β-estradiol was 96% in 2 minutes and the concentration determined less than 10 ng/L. In the same time, removal efficiency of Estrone was 95% and the concentration determined 8.5 ng/L (Table 3.).

Ozone Requirement for an effective removal of both hormones was found 14 mg/L (Fig. 2 and Fig. 3.). However, in the wastewater effect of ozonation by products should also be considered (Bila et al., 2007).

**Acknowledgment**

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**References**


Recycling of Waste Materials in Asphalt Mix

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Keywords: Pavement, crushed glass, bitumen, rubber, waste tires, and stability

Abstract

With the continuously increased consumption, a large amount of waste materials is generated in the world. Asphalt modification can be made at different stages of its usage, from binder production to asphalt pavement production. The main objective of this paper is to study the change in asphalt mixture properties after adding two types of waste materials separately (waste tires rubber and waste car windshields glass). In the first experiment percentage of bitumen is replaced with melted waste tire rubber, while a fraction of fine aggregate is replaced with waste crushed glass in the second trial. The results showed that properties of modified asphalt are improved in comparison with normal asphalt pavement. The suitable amount of added rubber or glass was found to be 10% by bitumen or aggregate weight.

1. Introduction

The use of industrial additives in asphalt mixes will increase its cost. However, the use of alternative waste materials is less costly and eco-friendly, and is expected to enhance the asphalt properties (Mashaan, 2012). Enhancing asphalt properties will increase asphalt resistance to several pavement distress (Shu and Huang, 2014). Rubber and glass is widely used in our daily life, and with the continuously increased consumption, a large amount of waste from these materials is generated annually. The best way to deal with these wastes is to recycle and reuse them as raw materials or modifiers (Arnold et al., 2008).

Recycling these wastes can save energy and decrease environmental waste (Jony et al., 2011). Glass recycling can be made without changing its composition and properties (Gautam et al., 2012). Laboratory experiments showed that the strength and resistance to water damage of glass-asphalt pavement is higher than ordinary asphalt (Wu et al., 2004). In their study, Sajed and Shafabakhsh indicated that asphalt containing 10–15% crushed glass in surface course mixtures has been observed to perform satisfactorily (Shafabakhsh and Sajed, 2014).

In Australia, a road section was constructed using crushed glass in pavement mixes in 2010 (Waverley Council, 2010). A research study found that using tire rubber in asphalt mixture could decrease tire noise by approximately 50% (Zhu and Carlson, 2001). The study of Mashaan indicated that replacing 12% of bitumen weight by rubber will give higher asphalt stability (Mashaan et. Al, 2013). Hicks and Epps concluded that asphalt rubber pavement could be more cost effective than conventional pavement (Hicks and Epps, 2000). This paper examines the performance of asphalt in which a percentage of bitumen or aggregate is replaced with waste rubber or glass.
2. Material Methods

Conventional laboratory tests were conducted on bitumen and aggregate. Samples of tests results are shown in Table 1 below.

Table 1. Conventional Properties of Bitumen and Aggregate

<table>
<thead>
<tr>
<th>Test</th>
<th>Value</th>
<th>Test</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Penetration (0.1mm)</td>
<td>78.1</td>
<td>Wear percentage (Los-Angeles)</td>
<td>21.3%</td>
</tr>
<tr>
<td>Softening point (ºC)</td>
<td>52.3</td>
<td>Bulk Specific Gravity</td>
<td>3.00</td>
</tr>
<tr>
<td>Flashing point (ºC)</td>
<td>291</td>
<td>Apparent Specific Gravity</td>
<td>3.34</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.02</td>
<td>Absorption</td>
<td>5.15%</td>
</tr>
</tbody>
</table>

The conventional samples are prepared with 4.5%, 5%, and 5.5% bitumen percentage as shown in Table 2.

Table 2. Original Samples Preparation for Different Bitumen Percentage

<table>
<thead>
<tr>
<th>Aggregate Size</th>
<th>4.75mm</th>
<th>9.5mm</th>
<th>12.5mm</th>
<th>BITUMEN</th>
<th>TOTAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight (gram)</td>
<td>340.0</td>
<td>575.0</td>
<td>231.6</td>
<td>54 (4.5%)</td>
<td>1200.0</td>
</tr>
<tr>
<td>Weight</td>
<td>342.0</td>
<td>570.0</td>
<td>228.0</td>
<td>60 (5%)</td>
<td>1200.0</td>
</tr>
<tr>
<td>Weight</td>
<td>338.2</td>
<td>569.0</td>
<td>226.8</td>
<td>66 (5.5%)</td>
<td>1200.0</td>
</tr>
</tbody>
</table>

The crumb rubber from waste tires is melt in bitumen at 170º C and mixed with aggregate. On the other hand, waste car windscreen glass was crushed, and glass particles with diameter less than 4.75 mm were used in preparing the experiments. The mixture of aggregate and glass is heated to a temperature of 135 ºC before mixing with asphalt bitumen. All samples were compacted at temperature of 160 ± 5 ºC and subjected to 75 blows of compaction by Marshall Hammer on each side of specimen at temperature of 145 ºC.

Nine samples are prepared by mixing the melted rubber with bitumen at 5%, 10% and 15% of bitumen weight. Similarly, other nine samples are prepared by replacing the same mentioned percentages of fine aggregates with crushed glass.

3. Results and Discussion

The main objective of this paper was to examine the performance of asphalt in which a percentage of bitumen or aggregate is replaced with waste rubber or glass. The tests were conducted using the standard Marshall Apparatus. Stability of the prepared samples were recorded. Results are shown in Fig. 1, 2 and 3.
From above figures showed that stability of mixes varied clearly after adding rubber on opposite of glass addition. Comparing the results of stability for asphalt-glass mix with conventional mix showed that there is an improvement at 10% glass. Stability increased with rubber addition up to 10%, and decreases at higher percentages. At high percentage of bitumen (5% or more), average stability of asphalt without rubber is low compared to asphalt with 10% rubber. The results showed that the stability values increase with an increase in the bitumen content. The average values of Marshall Test stability with different added percentage were summarized in Table 3 below.
From above table, average stability of asphalt without rubber is higher in comparison with the asphalt with 5%, and 20% rubber, but lower than 10%. It is also appeared that the average stability increased with glass addition until the maximum level (approximately 10% of glass) then it started to decrease.

The above standards table (Table 4) indicated that all test values consistency minimum stability of Marshal Test (Asphalt Institute, 1997).

4. Results and Discussion

Stability was improved by adding rubber or glass to the asphalt pavement. The appropriate used percentage was 10%. The finding of this study agreed with other international studies.

Concerning the cost, several studies showed the high cost of modified asphalt. But it is more accurate to consider the design life cost of pavement not the initial construction cost. In this research article, a number of asphalt samples were examined on laboratory tests. The conclusions are summarized as follows.

1- Waste tires rubber and crushed glass can be used in asphalt pavement with optimum replacement ratio of 10%.

2- The average stability for 10% modified mixture was higher than the control mixture. Therefore, a significant improvement occurred in the Marshall properties of asphalt mixtures using a waste rubber or crushed glass modifier.

3- All test values are consistent with the specifications limits.

4- The results of this study apply only to the type of rubber that was used, and to the specific gradation and type of glass that was used. Other resources of rubber or glass may produce different results.
References

Recoverable Products from Biomass with Pyrolysis/Gasification Processes

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Key words: Biomass, Pyrolysis, Gasification

Abstract

Biomass energy is probably one of the most important resources that can meet ever-increasing need of the world for energy as a result of growing population and industrialization through sustainable ways and without polluting the environment. The examples of biomass can be given as follows; trees, plants specially cultivated such as corn, wheat, grass, moss, all organic leavings such as fruit and vegetable wastes, animal excreta, fertilizer and industrial wastes. In this study, various macroalgae species (three Chlorophyta, one Rhodophyta and one Phaeophyceae) collected from the coastal areas of Istanbul were assessed as biomass raw material and the research was conducted to reveal useful product output and energy recycling means though thermochemical (pyrolysis/gasification) methods. Pyrolysis experiments were conducted at 500 and 600 °C while gasification experiments were conducted at 600 and 700 °C. No synthesis gas having sufficient thermal value was found during pyrolysis tests. According to heating values of the synthesis gas obtained through gasification experiments, the highest heating value (HHV) reached to 1700 kcal/kg at 700 °C gasification conditions.

1. Introduction

Biomass is a renewable energy source not only because the energy in it comes from the sun, but also because biomass can re-grow over a relatively short period of time compared with the hundreds of millions of years that it took for fossil fuels to form. Through the process of photosynthesis, chlorophyll in plants captures the sun's energy by converting carbon dioxide from the air and water from the ground into carbohydrates-complex compounds composed of carbon, hydrogen, and oxygen. Biomass is considered to be a significant alternative energy resource since vegetative organisms last as long as sunlight exists (Yaman, 2004). Biomass contains stored energy. That's because plants absorb energy from the sun through the process of photosynthesis. When biomass is burned, this stored energy is released as heat. (URL 1).

Many different kinds of biomass, such as wood chips, corn, and some types of garbage, are used to produce electricity. Some types of biomass can be converted into liquid fuels called biofuels that can power cars, trucks, and tractors. Leftover food products like vegetable oils and animal fats can create biodiesel, while corn, sugarcane, and other plants can be fermented to produce ethanol (URL 2).

Biomass can be threatened in a number of different ways to provide such fuel. In general, such methods are divided into biological and thermal. The main thermal conversion processes are combustion, gasification and pyrolysis (Vigouroux, 2001). Pyrolysis is a thermo-chemical decomposition process in which organic material is converted into a carbon-rich solid and volatile matter by heating in the absence of oxygen. The solid, termed variously as char, biochar,
charcoal or coke, is generally of high carbon content and may contain around half the total carbon of the original organic matter (Brownsort, 2009). Gasification is an alternative thermo-chemical conversion technology suitable for treatment of biomass or other organic matter including municipal solid wastes or hydrocarbons such as coal. It involves partial combustion of biomass in a gas flow containing a controlled level of oxygen at relatively high temperatures (500-800°C) yielding a main product of combustible syngas with some char (Brownsort, 2009).

2. Materials and Methods

In this study, seaweed samples of 5 species (one red (Rhodophyta), one brown (Phaeophyceae) and three green (Chlorophyta) algae) collected from the coastal areas of Istanbul were assessed as biomass raw material and the research was conducted to reveal useful product output and energy recycling means through thermochemical methods. In the laboratory, algal materials (*Ulva lactuca*, Chlorophyta; *Ulva intestinalis*, Chlorophyta; *Cladophora albida*, Chlorophyta; *Ceramium rubrum*, Rhodophyta; *Phyllariopsis brevipes*, Phaeophyceae) were cleaned and rinsed with distilled water (Figure 1). The collected samples were initially dried at room temperature and all processes were conducted on dry mass.

Figure 1. Seaweed species (*Ulva lactuca*, Chlorophyta; *Ulva intestinalis*, Chlorophyta; *Cladophora albida*, Chlorophyta; *Ceramium rubrum*, Rhodophyta; *Phyllariopsis brevipes*, Phaeophyceae)

2.1. Analytical Procedure

Prior to pyrolysis and gasification process, moisture content, ash, combustion loss, solid matter content, elemental analysis and calorific value experiments were conducted on raw samples. These experiments were carried out according to Standard Methods. (SM 2540 B; SM2540 E).

Synthetic gas measurements were performed with ABB-AO2020 model continuous gas analyzer. CO, CO₂, H₂, CH₄, and O₂ amounts within the synthetic gases that were generated during pyrolysis and gasification processes were measured as volumetric percentage. Elemental analyses of the raw macroalga samples used in the study and the solid products obtained at the end of the experiments were performed. C, H, N and S amounts of the samples were determined through Thermo Scientific Flash 2000 CHN-S elemental analysis. Calorific value of solid products was analyzed with LECO AC500 bomb calorimeter. Approximate calorific values of producer gases were calculated according to H₂, CO and CH₄ volumetric percentages (Ozcan et al., 2016; Ongen et al., 2014; Bossel 2003) determined by AO2020 online gas analyzer.
2.2. Experimental Setup

Pyrolysis and gasification experiments were conducted in steel reactor with cyclone separator and fixed bed. The reactor which was used in the experiments is a stainless steel with vertical shape and is 50 cm in length and 7 cm in diameter. Heat requirement of the system was met indirectly via ceramic resistance. Experimental conditions which used in study summarized at Table 1.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Sample (g)</th>
<th>Temp. (°C)</th>
<th>Agent</th>
<th>Flow rate (L/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolysis</td>
<td>30</td>
<td>500</td>
<td>N₂</td>
<td>1</td>
</tr>
<tr>
<td>Pyrolysis</td>
<td>30</td>
<td>600</td>
<td>N₂</td>
<td>1</td>
</tr>
<tr>
<td>Gasification</td>
<td>30</td>
<td>600</td>
<td>Dried air</td>
<td>0.05</td>
</tr>
<tr>
<td>Gasification</td>
<td>30</td>
<td>700</td>
<td>Dried air</td>
<td>0.05</td>
</tr>
</tbody>
</table>

3. Results and Discussion

In beginning of the study, some physical and chemical properties of the biomass to be used in the study were determined. For this purpose, elemental and proximate analysis were performed. The results are given in Table 2.

<table>
<thead>
<tr>
<th>Proximate Analysis, %mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
</tr>
<tr>
<td>9.2</td>
</tr>
<tr>
<td>30.6</td>
</tr>
<tr>
<td>69.4</td>
</tr>
<tr>
<td>90.8</td>
</tr>
<tr>
<td>Ultimate Analysis, %mass</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>24.98</td>
</tr>
<tr>
<td>H</td>
</tr>
<tr>
<td>4.23</td>
</tr>
<tr>
<td>N</td>
</tr>
<tr>
<td>3.58</td>
</tr>
<tr>
<td>S</td>
</tr>
<tr>
<td>0.46</td>
</tr>
</tbody>
</table>

Liquid product (tar) and solid residue (char) collected at the end of pyrolysis experiments are given in Table 3. Table 4 represents elemental analysis and calorific value of liquid and solid products. Calorific value of raw macroalga sample was found 2757 kcal/kg.

<table>
<thead>
<tr>
<th>Table 3. Solid and liquid products obtained from pyrolysis/gasification procedures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiments</td>
</tr>
<tr>
<td>-------------</td>
</tr>
<tr>
<td>Pyrolysis</td>
</tr>
<tr>
<td>Pyrolysis</td>
</tr>
<tr>
<td>Gasification</td>
</tr>
<tr>
<td>Gasification</td>
</tr>
</tbody>
</table>
Table 4. Elemental analysis and calorific value of solid products from pyrolysis and gasification experiments

<table>
<thead>
<tr>
<th>Experiments</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>Kalorific Value (kcal/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw biomass</td>
<td>24.98</td>
<td>4.23</td>
<td>3.58</td>
<td>0.46</td>
<td>2757</td>
</tr>
<tr>
<td>Pyrolysis 500 ºC</td>
<td>15</td>
<td>-</td>
<td>0.82</td>
<td>-</td>
<td>1995</td>
</tr>
<tr>
<td>Pyrolysis 600 ºC</td>
<td>19</td>
<td>-</td>
<td>1.23</td>
<td>-</td>
<td>1258</td>
</tr>
<tr>
<td>Gasification 700 ºC</td>
<td>26.5</td>
<td>-</td>
<td>1.36</td>
<td>-</td>
<td>1803</td>
</tr>
</tbody>
</table>

In pyrolysis experiments; as expected, it was detected that the syngas was very low in the experiment conducted in 500 ºC temperature. No CH₄ and H₂ gases could be observed in this temperature. When the syngas analysis results of pyrolysis experiment conducted in 600 ºC were examined, it was observed that similar to the 500 ºC temperature. However, CH₄ gas came out in more amounts compared to 500 ºC. The highest level of CH₄ was found out 2%.

Gasification experiment conducted in 600 ºC, it was observed that CH₄ and H₂ gases increased as expected. While the highest value of CH₄ was measured 8%, the maximum level of H₂ was measured 8%. The increasing concentrations of these two gases led to an increase in the calorific value of the syngas as well. In 700 ºC gasification experiment; maximum values of CH₄ and H₂ were 7% and 25% respectively. According to heating values of the synthesis gas obtained through gasification experiments, the highest heating value (HHV) reached to 1700 kcal/kg at 700 ºC gasification conditions (Figure 2).

![Figure 2. Higher heating value (HHV) variations depending on gasification time](image)

According to the results, calorific value of the synthesis gas obtained through gasification processes was suitable for energy recovery. In addition, heating values of the solid matters
obtained through pyrolysis/gasification procedures (char) differed between 1258 kcal/kg and 2009 kcal/kg (Table 4). Considering solid and gas matters obtained through pyrolysis and gasification processes together, it was found that macroalgae samples can be used as an alternative energy resource and pyrolysis/gasification methods can be efficiently used for a useful product yield from biomass.

References


Removal of Humic Acid from Water Medium by Coagulation/Flocculation Technique: Low Dose Coagulant Performance

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Keywords: Drinking water treatment, humic acid, coagulation and flocculation technique, ferric chloride,

1. Introduction

In nature, degradation of plant materials result with highly recalcitrant colored substances called “humic materials” (Sawyer, C.N et. al, 2003). They have high molecular weight, unknown chemical structure but polymeric and phenolic character. In addition, excreta of humans and land animals can result to formation of humic materials. Improper treatment strategies may cause their escape from treatment facilities. They do not cause any hazard as they are but in chlorination processes they may form halogenated compounds which are highly toxic and carcinogenic. This study investigates the removal performance of humic acid molecules from synthetic waters by low dose ferric ions.

2. Materials and Methods

2.1 Materials

Humic acid was supplied from Sigma Aldrich and obtained from Tin Mühendislik Chemical Supplies and Laboratory Instruments, Turkey. Ferric chloride (FeCl\textsubscript{3}.6H\textsubscript{2}O), hydrochloric acid (HCl, 37\%) and sodium hydroxide (NaOH, pellets) have been purchased from Merck and supplied from Tin Mühendislik Chemical Supplies and Laboratory Instruments. Cellulose acetate 0.45 µm syringe filter was obtained from Membrane solutions and supplied from Dorhan Medical Cyprus. Distilled water was obtained from Sartorius 61316, and a 611 UV ultrapure water system was purchased from Sartonet, Turkey. Coagulation and flocculation tests were performed by Kemira Flocculator 2000.

2.2 Methods

1 gram of humic acid was weighed and placed in a 1-L volumetric flask. 0.01 M sodium hydroxide was prepared by dissolving 0.4 gram in 1-L distilled water. 0.01M sodium hydroxide was slowly added to the graduated flask containing humic acid up to 1-L level to give 1 g.L\textsuperscript{-1} stock humic acid solution. 2.4 gram FeCl\textsubscript{3}.6H\textsubscript{2}O (containing 0.5 gram of Fe\textsuperscript{3+}) weighed and placed in 500-ml graduated flask. 8.27 ml of 37\% hydrochloric acid (Molarity:12.08 M) was diluted to 500 ml to give 0.2 M concentration. 0.2 M hydrochloric acid was slowly added to FeCl\textsubscript{3}.6H\textsubscript{2}O containing graduated flask to give 1g.L\textsuperscript{-1} Fe\textsuperscript{3+} stock solution. The operation conditions for coagulation and flocculation process is given in Table 1.

Coagulation and flocculation experiments have been conducted in 600 ml aqueous solutions and 15 ml of samples were taken before and after the process for absorbance and turbidity
measurements. Absorbance readings were performed after the filtration of the samples by 0.45 µm filter.

Shimadzu 2450 UV-visible type of spectrophotometer is used for humic acid concentration measurement. The standard aqueous solutions of humic acid (0-50 mg.L\(^{-1}\)) and Fe\(^{3+}\) ions (1-20 mg.L\(^{-1}\)) were prepared and absorbance measurements were recorded (Table 2 and Table 3). Afterwards, a fixed dose of Fe\(^{3+}\) (1 mg.L\(^{-1}\)) has been added to each standard solutions of humic acid and absorbance readings were recored in order to reveal the interference of remaining Fe\(^{3+}\) ions on humic acid concentration measurements. (Table 4). The calibration curve was plotted after the substraction of Fe\(^{3+}\) absorbance from the humic acid absorbance values and its plot is given in Figure 1.

<table>
<thead>
<tr>
<th>Fe mg.L(^{-1})</th>
<th>HA mg.L(^{-1})</th>
<th>UV. at 254 nm</th>
<th>Theoretical absorbance</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.11</td>
<td>0.08</td>
<td>32</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>0.14</td>
<td>0.12</td>
<td>15</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>0.17</td>
<td>0.16</td>
<td>8</td>
</tr>
<tr>
<td>1</td>
<td>25</td>
<td>0.42</td>
<td>0.43</td>
<td>-2</td>
</tr>
<tr>
<td>1</td>
<td>50</td>
<td>0.78</td>
<td>0.82</td>
<td>-5</td>
</tr>
</tbody>
</table>

Table 1. Coagulation/Flocculation operation conditions

<table>
<thead>
<tr>
<th>Process Details</th>
<th>Mixing power (rpm)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast mixing</td>
<td>200</td>
<td>1</td>
</tr>
<tr>
<td>Slow mixing</td>
<td>15</td>
<td>25</td>
</tr>
<tr>
<td>Sedimentation</td>
<td>0</td>
<td>60</td>
</tr>
</tbody>
</table>

Table 2. HA conc. Reading by (UV- Absorbance at 254 nm ) at pH 3

<table>
<thead>
<tr>
<th>Concentration of HA (mg.L(^{-1}))</th>
<th>UV. at 254 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.06</td>
</tr>
<tr>
<td>5</td>
<td>0.11</td>
</tr>
<tr>
<td>10</td>
<td>0.16</td>
</tr>
<tr>
<td>25</td>
<td>0.49</td>
</tr>
<tr>
<td>50</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Table 3. Fe conc. Reading by (UV- Absorbance at 254 nm ) at pH 3

<table>
<thead>
<tr>
<th>Concentration of Fe (mg.L(^{-1}))</th>
<th>UV. at 254 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.04</td>
</tr>
<tr>
<td>2.5</td>
<td>0.06</td>
</tr>
<tr>
<td>5</td>
<td>0.16</td>
</tr>
<tr>
<td>10</td>
<td>0.42</td>
</tr>
<tr>
<td>20</td>
<td>0.90</td>
</tr>
</tbody>
</table>
3. Results and Discussion

3.1 pH Effect
It has been observed that neutral to alkaline conditions results with better turbidity and UV-254nm absorbance removal (Table 5). This range provided the best attraction between negatively charged surface of humic acid and Fe$^{3+}$ ions. In addition, the insoluble nature of Fe$^{3+}$ ions at neutral and alkaline pH conditions removed humic acid molecules along the way of its precipitation (Figure 2).

Table 5. Coagulation/Flocculation results for 50 mg.L$^{-1}$ humic acid with 17 mg.L$^{-1}$ Fe$^{3+}$ dosage under various pH conditions

<table>
<thead>
<tr>
<th>pH</th>
<th>Fe$^{3+}$ dose (mg.L$^{-1}$)</th>
<th>Humic acid concentration (mg.L$^{-1}$)</th>
<th>Before Coagulation/Flocculation and Sedimentation</th>
<th>After Coagulation/Flocculation and Sedimentation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Turbidity (NTU)</td>
<td>UV-Intensity at 254nm</td>
</tr>
<tr>
<td>Blank</td>
<td>0</td>
<td>50</td>
<td>6.2</td>
<td>1.26</td>
</tr>
<tr>
<td>9</td>
<td>15</td>
<td>50</td>
<td>7.8</td>
<td>1.12</td>
</tr>
<tr>
<td>7</td>
<td>15</td>
<td>50</td>
<td>7.2</td>
<td>1.05</td>
</tr>
<tr>
<td>6</td>
<td>15</td>
<td>50</td>
<td>8.0</td>
<td>1.17</td>
</tr>
<tr>
<td>5</td>
<td>15</td>
<td>50</td>
<td>7.6</td>
<td>1.15</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>50</td>
<td>11.4</td>
<td>0.62</td>
</tr>
</tbody>
</table>

Figure 1. Humic acid calibration curve

$$y = 0.0141x + 0.0663$$
$$R^2 = 0.9925$$
Figure 2. Coagulation/Flocculation tests for 50 mg.L\(^{-1}\) humic acid with 15 mg.L\(^{-1}\) Fe\(^{3+}\) dosage under various pH conditions

3.2 Fe\(^{3+}\) Dose Effect

The doses of Fe\(^{3+}\) used in this study varied between 1 – 15 mg.L\(^{-1}\). The results indicates that under the doses of 1-2.5 mg.L\(^{-1}\), flocs are formed after the interaction between Fe\(^{3+}\) and humic acid but they were not capable to come together because of the low attraction because of the low doses of coagulant therefore; no coagulation and precipitation was observed (Figure 3). This was observed from the increase in turbidity (Figure 4). After filtration of these samples UV-254nm absorbance removal was 18% and 85% for 1 mg.L\(^{-1}\) and 2.5 mg.L\(^{-1}\) Fe\(^{3+}\) doses, respectively. The maximum UV-254 nm absorbance removal occurred when Fe\(^{3+}\) doses were adjusted to 2.5 and 5 mg.L\(^{-1}\) (Figure 5). The results are given in Table 6.

Figure 3. Removal of 50 mg.L\(^{-1}\) Humic acid with coagulation and flocculation by different doses of Fe\(^{3+}\)
4. Conclusion
Coagulation and flocculation technique is widely used for surface and groundwater treatment applications. It is important to study the removal of emerging contaminants as well as non-
biodegradable, potential hazard causing natural compounds such as humic acid by this conventional treatment method.

In most surface waters humic acid concentration varies between 0-50 mg.L\textsuperscript{-1} [2]. In this study, 50 mg.L\textsuperscript{-1} humic acid containing aqueous solutions were subjected to low doses of ferric ion (1-15 mg.L\textsuperscript{-1}) in order to remove turbidity and UV\textsuperscript{-254nm} absorbance. It is observed that above 5 mg.L\textsuperscript{-1} Fe\textsuperscript{3+} dose, coagulation initiates and both turbidity and UV\textsuperscript{-254nm} absorbance removal can be achieved. This study further aims to combine pre and post ozonation with coagulation/flocculation process for the further removal of humic materials by mineralization.

References


Assessment and Investigation of Paracetamol from Wastewater By Using Oxidation Process and TOC

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*Environmental Engineering, Ondokuz Mayis University, Engineering Faculty, Samsun,

Keywords: Residual Pharmaceuticals, Paracetamol, Advanced Oxidation Processes, Water, Wastewater

Abstract

Pharmaceuticals are a group of organic compounds specifically designed to have a therapeutic effect on the human body at low concentrations. Paracetamol is a most widely used medicine in almost every part of word and present and used in almost every household. Removal of pharmaceuticals by water treatment is therefore an important issue. Conventional wastewater treatment plants are not enough to remove pharmaceuticals therefore advanced oxidation processes have become an emerging solution.

In the present study, under laboratory conditions, coagulation and advance oxidation, using H₂O₂ and FeSO₄ (Fenton process) is used to degrade the concentrations of paracetamol from water were conducted. We have taken 500mg/l paracetamol synthetic solution. Biodegradability of the treated solutions (COD) and test with background constituents in the water matrix, like TOC will also observed. In the end of the experiments, to measure the efficiency of Fenton process, optimum pH, FeSO₄, H₂O₂, stirring time, residence time and temperature will be measured. Before starting our experiments we checked initial values of COD, TOC and amount of paracetamol in untreated samples. Later, we selected different parameters like, pH values (2-6), FeSO₄ and H₂O₂ concentration (30-75-150 mg/l), stirring time (10, 20, 30 minutes), residence time (30, 60, 90 minutes) and room temperature that will be provided to our sample and optimal (high) values will be selected. After processing, 150 ml of samples was taken out from the upper layers of samples and COD and TOC tests were conducted.

1. Introduction

Pharmaceuticals are a group of organic compounds specifically designed to have a therapeutic effect on the human body at low concentrations. They have the ability to pass through cellular membranes and to persist being inactivated long enough in the body to have their desired effect (Bottoni et al., 2010) and later presence in the environment at low concentrations is an emerging challenge nowadays. Paracetamol is a most widely used medicine in almost every part of word and present and used in almost every household. Paracetamol is one of these pharmaceutical products commonly used for humans and animals as mild analgesics and anti-inflammatory, which is present in waste water treatment plant (WWTP) effluents as a result of its incomplete removal, or even in natural waters (Carrasco-Diaz et al, 2016). In addition, it can be transformed into toxic compounds by the chlorination process used in WWTP. Therefore, it is of high interest to develop efficient treatment processes for limiting the presence of paracetamol in aquatic environments. Waste water purification plants in general have not been designed to deal with such compounds, as a result of which many of these compounds and their metabolites can
be found in surface water and ground water (Heberer, 2002), and possibly end up in drinking water in low concentrations (Heberer, 2002; Benotti et al., 2009). Removal of pharmaceuticals by water treatment is therefore an important issue.

Conventional wastewater treatment plants are not enough to remove pharmaceuticals therefore advanced oxidation processes have become an emerging solution. Advanced oxidation processes AOPs can be broadly defined as aqueous phase oxidation methods based on the intermediacy of highly reactive species such as (primarily but not exclusively) hydroxyl radicals in the mechanisms leading to the destruction of the target pollutant. Because of the diversity of technologies involved and the areas of potential application AOPs are very popular. Key AOP involves heterogeneous and homogeneous photo catalysis based on the Fenton’s reagent. Depending on the properties of the micro-polluted to be treated AOP can be employed either alone or coupled with other physicochemical and biological processes. Process coupling is conceptually beneficial usually leading to improved treatment efficiencies (Maria et al., 2009).

2. Material Methods

In the present study, under laboratory conditions, coagulation and advance oxidation, using H2O2 and FeSO4 (Fenton process) is used to degrade the concentrations of paracetamol from water were conducted. We have taken 500mg/l paracetamol synthetic solution. Biodegradability of the treated solutions (COD) and test with background constituents in the water matrix, like TOC will also observed. In the end of the experiments, to measure the efficiency of Fenton process, optimum pH, FeSO4, H2O2, stirring time, residence time and temperature will be measured. Before starting our experiments we checked initial values of COD, TOC and amount of paracetamol in untreated samples. Later, we selected different parameters like, pH values (2-6), FeSO4 and H2O2 concentration (30-75-150 mg/l), stirring time (10, 20, 30 minutes), residence time (30, 60, 90 minutes) and room temperature that will be provided to our sample and optimal (high) values will be selected. After processing, 150 ml of samples was taken out from the upper layers of samples and COD and TOC tests were conducted.

2.1. Analysis of drug (paracetamol)

A solution of paracetamol, obtained from market was prepared in tap water to carry out Advance oxidation with fenton process. in the experiments, TAMOL namely tablet was used to obtain 500mg/l paracetamol content. For the preparation of sample, tablet conaining 500mg paracetamol tablet was first finely grinded to powderd form and then mixed with tap water in 1 liter flask to prepare 500mg drug/liter solution.

2.2. Instrumentation and chemicals

We used in fenton process 35% pure grade H2O2 hydrogen peroxide (Merck), FeSO4.7H2O iron sulphate (Sigma Aldrich), 98% pure grade H2SO4 (Merck), NaOH (Merck). We used in COD process potassium dichromate K2CrO4 (Merck), Iron ammonium sulphate (Carlo Erba) 99% pure grade 1.10-phenanthroline and monohydrate (Sigma Aldrich), mercury sulphate (sigma aldrich), silver sulphate (sigma aldrich), thermoreactor (spectroquant TR 320). We used in TOC analyze Apollo 9000 combustion TOC analyizer.

2.3. Fenton process

The purpose of this study is to analyse the optimum degradation of paracetamol by using different parameters like pH, temperature, stirring time, waiting time, amount of Iron
Iron sulphate and hydrogen peroxide.

![Figure 1. Fenton process system.](image)

In this context, first of all experiment with different pH like 2,3,4 and 6 was performed with concentrations: 75mg/l; FeSO$_4$; 75ml/l; H$_2$O$_2$; stirring time;20 minutes, waiting time 60 minutes. After measuring COD and TOC optimum pH was observed to be in between 3 and 4. Because the value was more closer to 3 and after consulting literature further experiments were decided to carry out by taking 3.5 pH as optimum (Li et al., 2012). Values and results of TOC and COD can be cross checked from table 1 and figure 2.

Table 1. PRC removal with fenton process. H$_2$O$_2$:75 mg/L, Fe$^{2+}$: 75 mg/L, stirring time:20 min, waiting time:60 min

<table>
<thead>
<tr>
<th>pH value</th>
<th>Final concentration (COD) (mg/L)</th>
<th>Efficiency (COD removal (%))</th>
<th>Final concentration (TOC) (mg/L)</th>
<th>Efficiency (TOC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>960</td>
<td>31.81</td>
<td>294.03</td>
<td>13.64</td>
</tr>
<tr>
<td>3</td>
<td>704</td>
<td>50</td>
<td>264.22</td>
<td>22.40</td>
</tr>
<tr>
<td>4</td>
<td>896</td>
<td>36.36</td>
<td>280.95</td>
<td>17.48</td>
</tr>
<tr>
<td>6</td>
<td>1024</td>
<td>27.27</td>
<td>312.40</td>
<td>8.25</td>
</tr>
</tbody>
</table>

(Initial ph:7.47, Initial COD: 1408 mg/L, Initial TOC concentration: 340,50 mg/L C)

![Figure 2. PRC removal with fenton process. Efficiency with COD and TOC.](image)

In the second step optimum concentration of FeSO$_4$ required for the degradation of drug was analysed. For this purpose with optimum pH of <3.5; 75 mg/L; H$_2$O$_2$; stirring time:20 minute, waiting time 60 minute, different concentrations of FeSO$_4$ like, 30-75-150 mg/L were tried to select optimum amount to carry out further series of steps. As per the observed results of COD and TOC best value of FeSO$_4$ was 75 mg/L. Values and results of TOC and COD can be seen in table 2 and figure 3.
Table 2. PRC removal with fenton process. Ph<3.5, H₂O₂:75 mg/L, stirring time:20 min, waiting time:60 min

<table>
<thead>
<tr>
<th>Fe²⁺ Concentration (mg/L)</th>
<th>Final concentration (COD) (mg/L)</th>
<th>Efficiency (COD removal (%))</th>
<th>Final concentration (TOC) (mg/L)</th>
<th>Efficiency (TOC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>800</td>
<td>43.18</td>
<td>380.95</td>
<td>17.48</td>
</tr>
<tr>
<td>75</td>
<td>704</td>
<td>50</td>
<td>264.22</td>
<td>22.40</td>
</tr>
<tr>
<td>150</td>
<td>706</td>
<td>49.50</td>
<td>270.53</td>
<td>20.54</td>
</tr>
</tbody>
</table>

(Initial ph:7.47, Initial COD: 1408 mg/L, Initial TOC concentration: 340.50 mg/L C)

The purpose of third step was selection of optimum value of \( \text{H}_2\text{O}_2 \). In this step different concentrations of \( \text{H}_2\text{O}_2 \) like 30-75-150 mg/L were tried with optimum pH<3.5, optimum value of \( \text{FeSO}_4 \) 75 mg/L along with stirring time; 20 minute, waiting time 60 minute. According to the observed values of COD and TOC optimum value of \( \text{H}_2\text{O}_2 \) was selected as 150 mg/L. Published literature has show that degradation of drugs increases with the increase amount of \( \text{H}_2\text{O}_2 \), hence increased amount of \( \text{H}_2\text{O}_2 \) means good degradation (Kang and Hwang, 2000).

After these results we assumed that our research is on right track. Observed TOC and COD values and results are shown in table 3 and graph 4.

Table 3. PRC removal with fenton process. pH<3.5, Fe²⁺: 75 mg/L, stirring time:20 min, waiting time:60 min

<table>
<thead>
<tr>
<th>H₂O₂ Concentration (mg/L)</th>
<th>Final concentration (COD) (mg/L)</th>
<th>Efficiency (COD removal (%))</th>
<th>Final concentration (TOC) (mg/L)</th>
<th>Efficiency (TOC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>1088</td>
<td>22.78</td>
<td>298.95</td>
<td>12.20</td>
</tr>
<tr>
<td>75</td>
<td>704</td>
<td>50</td>
<td>264.22</td>
<td>22.40</td>
</tr>
<tr>
<td>150</td>
<td>64</td>
<td>95.45</td>
<td>202.64</td>
<td>40.48</td>
</tr>
</tbody>
</table>

(Initial ph:7.47, Initial COD: 1408 mg/L, Initial TOC concentration: 340.50 mg/L C)
In the fourth step the optimum stirring time was figured out by applying different stirring times of 20-30-60 minutes to the solution under optimized parameters: pH<3.5, 75 mg/L; FeSO₄, 150 mg/L; H₂O₂, waiting time 60 minutes. COD and TOC showed that 30 minutes is the best optimum stirring time. Values of TOC and COD are showed in table 4 and final results are showed in figure 5.

<table>
<thead>
<tr>
<th>Stirring time (min)</th>
<th>Final concentration (COD) (mg/L)</th>
<th>Efficiency (COD removal %)</th>
<th>Final concentration (TOC) (mg/L)</th>
<th>Efficiency (TOC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>72</td>
<td>94,88</td>
<td>213,86</td>
<td>37,19</td>
</tr>
<tr>
<td>20</td>
<td>64</td>
<td>95,45</td>
<td>202,64</td>
<td>40,48</td>
</tr>
<tr>
<td>30</td>
<td>64</td>
<td>95,45</td>
<td>201,83</td>
<td>40,72</td>
</tr>
</tbody>
</table>

(Initial pH:7.47, Initial COD: 1408 mg/L, Initial TOC concentration: 340,50 mg/L C)

Fifth step was to optimize the waiting time, for this purpose time directions 30-60-90 minutes were provided to solution with other already optimized parameters as described above. Final optimized waiting time was cross checked by performing COD and TOC tests and it was finalized that waiting time of 60 minute was best optimum time. Observed TOC and COD values and results are shown in table 5 and graph 6.
**Table 5.** PRC removal with fenton process. H$_2$O$_2$: 150 mg/L, Fe$^{2+}$: 75 mg/L, stirring time: 20 min

<table>
<thead>
<tr>
<th>Settling time (min)</th>
<th>Final concentration (COD) (mg/L)</th>
<th>Efficiency (COD removal (%))</th>
<th>Final concentration (TOC) (mg/L)</th>
<th>Efficiency (TOC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>72</td>
<td>94.88</td>
<td>214.63</td>
<td>39.96</td>
</tr>
<tr>
<td>60</td>
<td>64</td>
<td>95.45</td>
<td>201.83</td>
<td>40.72</td>
</tr>
<tr>
<td>90</td>
<td>60</td>
<td>95.73</td>
<td>200.62</td>
<td>41.08</td>
</tr>
</tbody>
</table>

(Initial pH: 7.47, Initial COD: 1408 mg/L, Initial TOC concentration: 340.50 mg/L C)

**Figure 6.** PRC removal with fenton process. Efficiency with COD and TOC.

3. Results and Discussion

All the results for investigated tap water sample containing drug (paracetamol) are precisely described below: pH<3.5, FeSO$_4$: 75 mg/L, H$_2$O$_2$: 150 mg/L, stirring time: 30 minute, waiting time: 60 minute were optimized. According to these results highest removal efficiencies for COD and TOC are 95.45 and 40.72 % respectively. Observed values of pH and H$_2$O$_2$ are in agreement with the published literature. But on the other hand high concentrations of paracetamol in sample is because of lower concentration of chemicals provide for degradation. So increased amount of FeSO$_4$ and H$_2$O$_2$ is required or lesser amount of paracetamol should be added to the sample while preparation of stock solution.

In this study optimum values for the degradation of drug in the tapwater with the help of fenton process were investigated. After the careful analysis of results it could be concluded that fenton process is an easy, unexpensive advance oxidation process for the removal/degradation of pharmaceutical pollution from wastewater or freshwater resources.

**References**


Life Cycle Assessment as a Decision Support Tool in Wastewater Treatment Plant Design with Renewable Energy Utilization and Water Recycling-Reuse

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Keywords: environmental impacts, life cycle assessment, photovoltaic panels, scenario analysis, wastewater treatment

Abstract

This study summarizes how the Life Cycle Assessment (LCA) approach was used as an analysis and decision support tool to formulate and finalize a Biological Wastewater Treatment Plant (BioWWTP) design to serve not only for its primary goal of treating wastewater, but also for providing an integrated engineering solution to today’s multi-dimensional environmental problems and offering a public service installation serving for the well-being of the society and the environment as a whole. For that, sequential phases of LCA were implemented, various cases were structured, multiple scenarios were tested, scenario analyses were conducted and results were comparatively evaluated. In one of the main cases tested (Case-1), results implied that placing photovoltaic panels over the biological treatment units to meet 60% of the electricity demand of the system helped, i.e., reduce the global warming potential, hence the carbon footprint of the WWTP by 50%, in addition to mediating the use of a renewable energy source and enabling rainwater harvesting for water recycling-reuse, thus contributing to the sustainability of the entire installation.

1. Introduction

Life cycle assessment (LCA) is generally implemented using a “product based” evaluation approach (Dong, 2011). However, with the increasing concerns about “water scarcity” all around the world and the negative environmental impacts of energy consumption; recycling-reusing the resources and exploring the possibilities of decreasing energy demand and/or shifting to energy generation from renewable resources, have become other focal points of LCA, i.e., in the water sector. In this context, LCA has been implemented to wastewater treatment (WWT) practices since the ’90s, to link the treatment processes -of wastewater and sludge- to environmental impacts, to determine risks, and to use the forecasted results in selecting the best-case scenario in terms of feasibility and environmental impacts (Lorenzo-Toja et al., 2016). Such detailed LCAs in the water sector are rare in Turkey -if present for the currently operating full-scale WWTP. Accordingly, this study summarizes how the LCA approach was implemented and used as an analysis and decision support tool to formulate and finalize a full-scale Biological Wastewater Treatment Plant (BioWWTP) designed for Bartın Province, Black Sea Region, Turkey, including the concepts of energy generation from solar power and recycling-reusing the wastewater/rainwater, in addition to eliminating high risks of eutrophication in the Black Sea and overcoming the difficulties in sustainable nutrient removal due to severe weather conditions, marked by heavy rainy seasons and unexpected extreme storms, floods, etc.
2. Material and Methods

Main Approach: The methodology followed for conducting the LCA for the Bartin BioWWTP is presented in Figure 1. The frameworks and standards set in the ISO 14040 and ISO 14044 were followed (ISO 14040:2006 and ISO 14044:2006).

**Focus:** Main goal of implementing the LCA in Bartin’s BioWWTP design was to reveal the potential environmental risks of the system and to determine the best-case scenario in terms of environmental sustainability, while meeting the treatment efficiency and feasibility targets. In this context, the following impact categories, of which some have been listed as being widely-used in life cycle impact assessments (Heijungs and Guinee, 2012), were selected: abiotic depletion, global warming potential, ozone layer depletion, toxicity, fresh water and marine aquatic eco-toxicity, terrestrial eco-toxicity, photochemical oxidation, acidification, and eutrophication (Figure 1).

**Tools:** The following sections of the final step of LCA (implementation and evaluation) were executed by running numerical analyses: consistency- and completeness- checks and contribution-, comparison-, sensitivity-, and uncertainty-analyses. The scenarios generated for each structured case (total of 3 cases) were then tested with the aid of a commercially available software -SimaPro LCA Package and the life cycle inventory (LCI) database integrated in the software (SimaPro and ecoinvent, 2016).

3. Results and Discussion

System boundaries determined for the LCA are schematically presented in Figure 2 together with the inventory analysis for the main units of the system -the BioWWTP and the sludge management parts-, as well as the innovative engineering solutions comprised of photovoltaic panels designed for the dual purpose of electricity generation from solar power and rainwater harvesting. Two interconnected sub-systems, namely the natural conveyance system and the recreational pond, were not included in LCA, since those were determined to have no adverse environmental effects: the natural conveyance system was structured to collect the rainwater from the catchment area, pavements, roads, as well as that harvested from the photovoltaic panels located on the biological treatment units and to convey the flow to the recreational pond;
the latter designed for recreational purposes but also providing storage of treated wastewater for future reuses, contributing to additional removal of pollutants by the help of aquatic plants; and thus together providing water recycling-reusing and amending dissolved oxygen level in the final receiving water body; the Black Sea.

Total of three cases with multiple scenarios were generated and the LCA analyses were conducted for all those options summarized in Table 1. Modeling and simulations were conducted by using the SimaPro software and the simulation results of all scenarios obtained from the program were comparatively evaluated for the cases.

**Table 1.** Cases and scenarios tested by using the SimaPro

<table>
<thead>
<tr>
<th>Case-1</th>
<th>Construction and use of photovoltaic panels covering the main BioWWTP units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scenario-1: dual source for electricity: 60% from photovoltaic panels + 40% from the main grid</td>
<td></td>
</tr>
<tr>
<td>Scenario-2: mono source for electricity: 100% from the main grid</td>
<td></td>
</tr>
<tr>
<td>Case-2</td>
<td>Transportation of the treated sludge to cement factory</td>
</tr>
<tr>
<td>Scenario-1: transportation to a cement factory 6 km away from the WWTP</td>
<td></td>
</tr>
<tr>
<td>Scenario-2: transportation to a cement factory 100 km away from the WWTP</td>
<td></td>
</tr>
<tr>
<td>Scenario-3: transportation to a cement factory 500 km away from the WWTP</td>
<td></td>
</tr>
<tr>
<td>Scenario-4: transportation to a cement factory 1000 km away from the WWTP</td>
<td></td>
</tr>
<tr>
<td>Case-3</td>
<td>Use of chemicals as an aid for sludge dewatering</td>
</tr>
<tr>
<td>Scenario-1: use of polyelectrolytes as sludge dewatering aid</td>
<td></td>
</tr>
<tr>
<td>Scenario-2: use of ferric chloride as sludge dewatering aid</td>
<td></td>
</tr>
</tbody>
</table>
Interpretation of the Results / Scenario Outputs
Case-1: “Construction and use of photovoltaic panels covering the main BioWWT units

Simulation results obtained from SimaPro and showing the environmental impacts of the two tested scenarios of Case-1 are presented in Figure 3.

As seen from Figure 3; (i) the two scenarios are no different from each other in terms of their contribution to “eutrophication”, (ii) use of electricity partly from the photovoltaic panels (scenario-1) has a slightly higher contribution to “ozone layer depletion”, mainly due to the impact of production and construction processes of the photovoltaics, and (iii) scenario-1 (60% electricity from photovoltaic panels and 40% from the main grid) has considerably lower negative impacts in all other impact categories. As apparent from the results of those scenario tests, scenario-1 was determined to have a marked advantage over scenario-2 in terms of decreasing the probable adverse environmental impacts of the designed public installation. Accordingly, the overall final interpretation of the detailed LCA was adopted as a decision support input to finalize the design and feasibility study of Bartin’s BioWWTP including photovoltaic panels covering main biological treatment units and generating electricity for on-site use. As briefly stated above, the other prominent advantage of the photovoltaic panels was to use those to collect rainwater for recycling and to prevent interference of the latter with the biological processes; altogether contributing to the overall sustainability of the system.

Case-2: Transportation of the treated sludge to cement factory

Last step of sludge management was transportation of the on-site treated waste activated sludge to a cement factory (Figure 2) to be used there as fuel-additive. It was required to consider the probable risks that might arise from involvement of such an external stakeholder. Accordingly, environmental risks/impacts of transporting the treated sludge to different cement factories at different distances from the treatment site (Table 1) were analyzed using the simulation software. Results of the scenario tests showed that there was no apparent difference - in terms of contribution to Global Warming Potential; CO₂ eq.- between transporting the treated sludge to cement factories located 6 km or 100 km away from the plant, and both options were
significantly advantages in terms of decreasing the negative impacts in “ozone layer depletion” and “terrestrial eco-toxicity” categories compared to the other scenarios.

*Case-3: Use of chemicals as an aid for sludge dewatering*

The two scenarios structured for Case-3 were using polyelectrolytes (scenario-1) vs ferric chloride (scenario-2) as chemical aids for sludge dewatering in sludge management. Scenario tests showed that there is no obvious difference between those two options in terms of their contribution to any of the considered impact categories. Consequently, those chemicals were to be used interchangeably, if needed, without compromising on sustainability.

As presented above, implementation of LCA, enriched by numerical analyses and/or software simulations, is a powerful and reliable decision support tool in WWTP design and feasibility studies, especially when to offer innovative engineering solutions, such as those presented here as using photovoltaic panels for energy generation from renewable resources and for collecting rainwater to be recycled.

**References**


Current Waste Electrical and Electronic Equipment (WEEE) Collection Performance in Turkey

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Keywords: Waste Electrical and Electronic Equipment (WEEE), WEEE collection targets, WEEE regulation, white goods

Abstract

Efficient management of waste electrical and electronic equipment (WEEE) mainly depends on the accuracy of the predictions of the amounts of WEEE to be collected. In Turkey the collection targets for electrical and electronic equipment (EEE) manufacturers has been set by the current regulation enacted in 2013 and the collection targets were revised in 2015 since the collection targets could not be defined for each EEE manufacturer due to the lack of a coordination center. The predicted amounts were not realistic and the revision of the current regulation is on the way. In order to predict WEEE amounts accurately, current collection performance should be analyzed in detail. This study presents the inventory of WEEE collection in Turkey for the period of November 2015-February 2016.

1. Introduction

Waste Electrical and Electronic Equipment (WEEE) is one of the most important type of waste which has to be managed properly due to the hazardous components and yet has extremely valuable content when recycled appropriately. In this context, EU WEEE Directive was recast as Directive 2012/19/EU in 2012 (WEEE, 2012) since a number of substantial changes were to be made to Directive 2002/96/EC (WEEE, 2002).

Although the economic value of WEEE has been widely recognized there are still challenges in the management of WEEE. One of the most critical points for the development of sustainable strategies for WEEE recycling is the prediction of the type and amount of WEEE generated. There is scarce amount of data accumulated globally on the and there is hardly any data on WEEE generation in Turkey.

Ministry of Environment and Urbanization (MoEU) is responsible for the regulation of collection and recycling of WEEE and Regulation on Waste Electrical and Electronic Equipment (TR WEEE, 2012) has been published in the Official Gazette No: 28300 and was enacted on 22.05.2012. The regulation manages the responsibilities of all actors and stakeholders for the manufacturing of Electrical and Electronic Equipment (EEE) and for the collection and recycling of WEEE. In this respect EEE manufacturers are obliged to collect and recycle certain amounts of WEEE. However, the collection targets were revised in 2015 and further revision is foreseen with a new regulation drafted in 2016 (TR WEEE draft, 2016).

This study presents the actual WEEE collection amounts for the period of November 2015 and February 2016. It is the first and only document where real data for Turkey is generated. The data presented includes types and amounts of WEEE collected from different regions of Turkey.
by Electrical and Electronic Recycling and Waste Management Association, municipalities and manufacturers’ repair services.

2. Material Methods

Electrical and Electronic Recycling and Waste Management Association has been founded in 2014 in order to fulfill the legal requirements of EEE manufacturers. Currently 29 of the biggest manufacturers are members of ELDAY and therefore ELDay is one of the main actors in WEEE management. The Association-own Enterprises (Elektrik ve Elektronik Geri Dönüşüm ve Atık Yönetimi Derneği İktisadi İşletmesi, ELDAY, www.elday.org) is responsible for the collection and recycling of WEEE.

3. Results and Discussion

3.1. Proposed Draft Regulation for WEEE Collection Targets in Turkey

Current Turkish WEEE Regulation (TR WEEE, 2012) sets increasing collection targets starting from 0.3 kg/ca.year in 2013 up to 4 kg/ca.year in 2018. Although the targets for 2013 and 2014 were achievable, as they increased to 1 kg/ca.year for household WEEE, they could not be achieved by the EEE manufacturers.

After the negotiations MoEU has revised the targets and defined them in terms of production percentages of the previous year instead of amount per capita (MoEU, 2015), i.e. a manufacturer producing refrigerators will collect and recycle 4.25% of their 2014 production in 2015. MoEU has also prepared a new regulation (TR WEEE draft, 2016) and announced the draft regulation to get the opinion of the stakeholders and it is possible to have even reduced collection amounts with the new regulation.

The change in the regulation and especially the collection targets is unfortunately due to the deficiency of data about the inventory of WEEE in Turkey. The WEEE target amounts in the current legislation were set based on WEEE data from Europe, however WEEE generation varies regionally in terms of WEEE types and amounts. Therefore one of the crucial points in WEEE management is WEEE inventory and prediction of future amounts on a regional scale.

The revised collection amounts for the period 2013-2015 as announced by MoEU (2015) is also present in the draft regulation as given in Table 1 and the increasing percentages for collection targets of the manufacturers is set as given in Figure 1.
Table 1. Collection targets set for the period before 01/01/2016 by draft Turkish WEEE Regulation.

<table>
<thead>
<tr>
<th>EEE Categories</th>
<th>Collection Target (kg/ca-year)</th>
<th>Percent (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.Refrigerators/Freezers/Air conditioning equipment</td>
<td>0.05 / 1.25</td>
<td>0.09 / 2.25</td>
</tr>
<tr>
<td></td>
<td>0.17 / 4.25</td>
<td></td>
</tr>
<tr>
<td>2.Large White Goods (except refrigerators/freezers/air conditioning equipment)</td>
<td>0.1 / 2.5</td>
<td>0.15 / 3.75</td>
</tr>
<tr>
<td></td>
<td>0.32 / 8</td>
<td></td>
</tr>
<tr>
<td>3.TVs and monitors</td>
<td>0.06 / 1.5</td>
<td>0.10 / 2.5</td>
</tr>
<tr>
<td></td>
<td>0.22 / 5.5</td>
<td></td>
</tr>
<tr>
<td>4.IT and telecommunication equipment (except TVs and monitors)</td>
<td>0.05 / 1.25</td>
<td>0.08 / 2</td>
</tr>
<tr>
<td></td>
<td>0.16 / 4</td>
<td></td>
</tr>
<tr>
<td>5.Luminaires</td>
<td>0.01 / 0.25</td>
<td>0.02 / 0.5</td>
</tr>
<tr>
<td></td>
<td>0.02 / 0.5</td>
<td></td>
</tr>
<tr>
<td>6.Small household appliances, electrical and electronic equipment, toys, sports</td>
<td>0.03 / 0.75</td>
<td>0.06 / 1.5</td>
</tr>
<tr>
<td>and leisure equipment, monitoring and control equipment</td>
<td>0.11 / 2.75</td>
<td></td>
</tr>
<tr>
<td><strong>TOTAL HOUSEHOLD WEEE (kg/ca-year)</strong></td>
<td><strong>0.3</strong></td>
<td><strong>0.5</strong></td>
</tr>
<tr>
<td></td>
<td><strong>1</strong></td>
<td></td>
</tr>
</tbody>
</table>

Figure 1. Increasing collection targets of WEEE.

ELDAY, representative of the five biggest EEE manufacturers, has declared that they are mainly pleased with the new collection targets based on the production amounts of the previous year starting from 2016 in the draft version of the revised regulation (TR WEEE draft, 2016), which they find appropriate for the realities in the country. However, the targets have been set for the upcoming fifteen years, i.e., 2016-2030 period. Collection based on the manufactured amounts is just applicable starting from 2016 and without any data on collection performances based on the produced amounts, the predictions for such a long period would not be accurate. ELDAY suggests that the revision of the targets every five years and setting the targets in the regulation
for the period of 2016-2021 for the time being would prevail a realistic approach for WEEE management.

3.2. WEEE Collection Performance
The available data shows that nearly 1,039 tons of WEEE has been collected by ELDAY in the period of November 2015 and February 2016. During the same period only 9 tons of WEEE could be collected by a municipality serving a population of 826,742 people (TÜİK, 2015) but WEEE amount of nearly 1,080 tons were secured at the manufacturers’ repair services. Thus a total of approximately 2,128 tons of WEEE were collected in four months. Taking the average and projecting the amount of 532 tons/month WEEE collection for 2015 the collected amount sums up to 6,384 tons/year which is on 8% of the target collection amount of 79,000 tons for 2015 based on the calculation using 1 kg/ca-year target. ELDAY represents approximately 50% of EEE production in Turkey and the inventory presented in this study represents country-wide WEEE collection of approximately 50% of the EEE manufacturers.

3.3. Inventory of the collected WEEE
The inventory presented in this study provides the detailed characterization of more than 1,000 tons of WEEE collected by ELDAY and the number of items and amounts for different groups of WEEE are presented. The regional variations of collected WEEE is also depicted in the study.

The percent distribution of different WEEE groups in terms of number of items is given in Figure 1. As shown in the figure refrigerators and washing machines are collected at the highest number while the number of goods like dishwashers, TVs/monitors and ovens is also significant.

![Figure 1. Number of collected WEEE.](image)

Shares of different WEEE in terms of weight is shown in Figure 2.
The distribution shows that the total weights of refrigerators and washing machines are the highest and dishwashers, also cover a significant portion. These three main white goods consisted of more than 90% of the total WEEE collected.

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TUIK 2015, https://biruni.tuik.gov.tr/medas/?kn=95&locale=tr
Harvesting Rainwater from Wastewater Treatment Plants: An Innovative Solution Serving both Mitigation and Adaptation for Climate Change

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Keywords: rainwater harvesting, climate change mitigation, climate change adaptation, photovoltaics,

Abstract

Priority of the study is new and innovative approaches about harvesting rainwater from wastewater treatment plants. Today, climate change impacts ecosystems and society. Increasing scarcity of water sources, water reuse will become necessary therefore energy consumption and water management are the main issues that should be given importance in wastewater treatment plants. In order to find effective solution for reducing the energy and water consumption and carbon dioxide generation, a system is designed for harvesting rainwater from wastewater treatment plants where photovoltaics, swale and an artificial lake are the main elements within the designed system.

1. Introduction

The wastewater generated from the central part of Bartın is discharged into sewage system but the wastewater from households is directly discharged into Bartın River without any treatment. Since the wastewater is discharged untreated, the water quality of the Bartın River decreases and this has adverse effects on living organisms. In conclusion, a treatment plant is required for Bartın center to protect the ecosystem and to provide the sustainability for the environment.

The adverse effects of contaminating parameters in wastewater can be roughly listed as; blockage in sewer system due to the water velocity decreases, anaerobic environment occurring by organic matter dissolution, dissolved oxygen depletion in receiving environment and extinction of bio-life, pathogen causing diseases, eutrophication as a result of retention of nutrients, apparent carcinogenic and mutagenic effects and toxicity.

The wastewater treatment plant design is aimed to annihilate these adverse effects and the risks related to wastewater to protect the public health and to sustain the hygiene of the public. It also aims to decrease the carcinogenic and mutagenic effects and toxicity that can be occurred due to the organic matter dissolution and oxygen depletion in receiving environment in the lack of treatment. To become sustainable; the wastewater treatment plant is designed which complies with the discharge standards for the generating wastewater and generating sludge thus natural sources are protected and development with the environment is provided.

Although generated wastewaters are domestic with no industrial discharges the design challenge is providing a sustainable nutrient removal process due to the availability of organic carbon in the treatment process. One of the main problems in Bartın is the high amount of rain with a monthly average of 89 kg/m², which results in lower retention times when raining, further reduction in organic carbon concentrations and considerable decrease in nutrient removal performance. In addition to the typical rainy characteristics of Bartın frequency and intensity.
of extreme weather events like storms and increased influences of flooding and draughts due to climate change makes it even harder to perform a stable and sustainable nutrient removal in Bartın WWTP.

2. Material Methods

In order to design Bartın WWTP the following steps have been followed:

- Population projection
- Estimation of flow rates for different conditions (wet and dry weather, minimum, maximum and peak flows)
- Wastewater characterization (based on the pollutant loads per capita)
- Comparison and selection of process alternatives
- Process configuration and unit design (Metcalf and Eddy, 2014)
- Cost estimation (investment costs and 30 year operating costs)

Design studies showed that nutrient removal could not be possible at the required level since organic carbon was not enough for both nitrogen (N) and phosphorous (P) removal. The process was designed as Johannesburg process where an additional anoxic tank was added in order to provide extra carbon from the endogenous decay of activated sludge in the return sludge tank as shown in Figure 1.

![Figure 1. Schematic presentation of Johannesburg process](image)

Designed process is capable of providing required N and P for average flowrates but has two major bottlenecks for the appropriate operation:

(i) **high energy costs** which would increase the water tariffs and would endanger affordability of high water bills by the public and thus would risk the coverage of operational costs.

(ii) **low treatment performance** due to addition of high amounts of rainwater, causing dilution of nutrients and decreasing hydraulic retention time and thus lowering reaction rates for wastewater treatment.

Two solution options were considered to overcome these bottlenecks: (i) using solar energy to produce electricity by photovoltaic cells, (ii) using panels to cover biological treatment units.
and collecting rainwater. Since photovoltaics require a large area (Soğukpınar and Bozkurt, 2015) it is not possible to construct them at each location. In order to provide an example for WWTPs with area constraints and to operate the system at the required efficiency innovative solutions for the mitigation of impacts of climate change have been suggested. Combination of the two requirements, i.e., electricity generation and prevention of rainwater intrusion to the biological units generated the innovative idea of using the photovoltaic cells as rainwater harvesting panels on the top of the activated sludge reactors.

3. Results and Discussion

Rainwater falling on the treatment plant basins are harvested using photovoltaics which can also serve for electricity generation to minimize carbon footprint of the plant as shown in Figure 2.

![Figure 2. Photovoltaic structures on WWTP basins used for rainwater harvesting](image)

In addition, measures have also been considered in the design for the adaptation for floods and draughts (Doğangönül and Doğangönül, 2009; IEA, 2001). Rainwater that falls on the ground and buildings is also collected and is transferred through a shallow rain swale (Figure 3) which is designed to be 8 m wide with side planes to control rain runoff in case of floods (Schueler, 1987; Fletcher et al., 2003).

![Figure 3. An example for a shallow rain swale used for rainwater harvesting](image)

Treated wastewater is stored in an artificial lake which serves as a reservoir both for overflows and a storage for water requirements to be reused in dry periods (Figure 4). The lake will be used for recreational purposes (Schueler, 1995). One third of the surface area of the artificial lake will be covered with aquatic plants and will also serve as a wetland for further nutrient removal prior to discharge (Zaimoğlu and Bozkurt, 2010; Gökalp et al., 2013). The lake is
designed to have a surface area of 4800 m$^2$ and volume of 3840 m$^3$ with an average retention time of 6-6.5 hours.

**Figure 4.** Artificial lake which serves as a water reservoir

The innovative design of Bartın WWTP has been proved to be economically feasible with features that will serve for the mitigation and adaptation measures for climate change. The approach used for rainwater harvesting and wastewater recycling and reuse will serve as a pioneering model for other similar WWTP designs.

**References**


An Assessment of Household Participation in Recycling Activities in Çankaya, Ankara

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Keywords: Packaging wastes, recycling, public participation, District of Çankaya, household.

Abstract

There is an increase in the production and consumption of packaging materials each day. This is mainly due to the industrial development and changes in the consumption habits of the community. The production and consumption cycles lead to degradation and damages in the environment. Even though a great number of national and international attempts were carried for the prevention of environmental problems, the active participation of public involvement in the process of recycling, particularly in Turkey, has been often neglected. Until recently, there has been neither enough attention given to recycling nor related activities of public participation in this process. These circumstances have resulted in mixing the recyclable materials with other wastes as well as lack of interests on cooperating with waste recycling process for years. The active participation of the community in the recycling process of the packaging wastes would contribute to the preservation of collected materials as well as reduction of environmental and economic damages to minimum. This participation also comes into prominence due to its contribution to the protection of urban aesthetics.

This study investigates the role of community in recycling process of packaging materials which have become a serious problem for the capital of Turkey, Ankara. In this respect, nine neighbourhoods in Çankaya District (Gaziosmanpaşa, Yukarı Bahçelievler, Çayyolu, Maltepe, Keklikpınarı, Zafertepe, Seyranbağları ve Yakupabdal) comprising low, medium and high income residing groups have been selected randomly. The questionnaire survey was carried out on approximately 430 households in order to evaluate and obtain results. The distinguishing features of those surveyed people, their behaviours and their motivation on this issue were considered in data collection. Here, the knowledge adequacy of households regarding recycling packaging material was considered. If knowledge was observed, the source of this information was investigated in detail. The level of information about the activities carried out by local administrations was also studied. The evaluation was done regarding the expectations on the accession of recycling containers in encouraging way during this process. The findings have been interpreted as a frequency distribution. As a result of assessment, it was observed that approximately 67% of households have information about the recycling process. However, the local administrations were found to not be enough affective in providing consciousness about the recycling.

1. Introduction

According to United Nations Environment Programme (UNEP), removing the solid wastes is one of the most important problems in the populated world that is caused by urban industrial
development processes. Many of countries in the world confront with this conflict and need a comprehensive and applicable solution in due (UNEP, 2005). According to the 21st agenda of UN Conference on Environment and Development held in Rio de Janeiro in 1992, if necessary enterprises are not achieved about wastages, there will be a considerable raise for the total volume of residuum (four or five times as much) until 2025. This increase will be much affected by the huge change in the world population which will rise to more than 8.5 billion in 2025 (Agenda 21, 1992).

In the world and in our country too, more than 70% of the people are living in the cities and this number is growing day by day (Cohen, 2006; TUIK 2015). Majlesi (2007) stated that there are more than one billion living in Asian countries and it is anticipated that their population will be more than four billion until 2050 which about half of them will accommodate in the cities. It is expected that 180 million tons of waste per day will be produced.

At the present time and in Adana and Mersin, around 3800-4000 tons of wastages are produced in one day which will be about 1.5 millions tons per year (Altuntop et al., 2014). Studies and related analysis indicate that annually 26 millions of solid residuum is produced in Turkey, 20% of that is packaging wastes and 80% organic waste and other kinds of residuum (Bülbü, 2013). There are about 5 million populations in Ankara that generate 3.5 millions of solid wastes per year, about 50% of that is packaging wastes (CDR, 2012).

In the world, particularly in developing countries, the increasingly growth of population on one hand and continuous expanding of the residential areas, changing in people’s life style and raising up the industrial and commercial utilities on the other hand, caused producing a huge amount of residuum, especially packaging wastes in the cities where because of the lack of knowledge and management weakness and absence of public involvement (Brunner & Fellner, 2007; Wilson, 2007; Blight, 2008).

Nowadays, discharging and repelling the packaging wastes in large and populated cities have caused several difficulties rendering other increasing problems. Apart from the imposed high cost expenditures to the country which is mostly because of collecting, transporting, repelling and discharging the residuum and wastages of the city, the environmental damages are also some serious problems (Loukil & Rouached, 2012) in a near future which we will confront with. It seems that recycling these kinds of products and returning them to market would be a suitable remedy by preserving renewable resources and protecting non-renewable resources as well as encouraging people to perform some efforts on recyclable materials (Pearce & Turner, 1990; Cherubini et al., 2008).

Some of the studies done so far showed that public participation in recycling process is correlated with their knowledge of how, where and what to recycle as well as their knowledge of how recycling contribute to environment (Folz, 1999; Tucker, 1999; Barr et al., 2003; McDonald & Oates, 2003, Kaplowitz et al., 2009). Even though a great number of national and international attempts were carried for the prevention of environmental problems (Bowonder, 1986; Grob, 1995; Steel, 1996), the active participation of public involvement in the process of recycling, particularly in Turkey, has been often neglected. Until recently, there has been neither enough attention given to recycling nor related activities of public participation in this process. These circumstances have resulted in mixing the recyclable materials with other wastes as well as lack of interests on cooperating with waste recycling process for years. The active
participation of the community in the recycling process of the packaging wastes would contribute to the preservation of collected materials as well as reduction of environmental and economic damages to minimum. This participation also comes into prominence due to its contribution to the protection of urban aesthetics.

In this study, the role of community in recycling process of packaging materials which have become a serious problem for the capital of Turkey was investigated. In this respect, nine neighbourhoods in Çankaya District comprising low, medium and high income residing groups were analyzed to their behaviours and their motivation on participating on recycling packaging waste issues.

2. Material Methods

This study was carried out in Çankaya, the central metropolitan district of the city of Ankara, and an administrative district of Ankara Province (Figure 1). The study material was a questionnaire form used in determining the knowledge of households living in Çankaya District about recycling process of packaging wastes and related recycling aspects

For this purpose, nine different neighbourhoods (Gaziosmanpaşa, Yukarı Bahçelievler, Çayyolu, Maltepe, Keklikpınarı, Zafertepe, Seyranbağları ve Yakupabdal) from Çankaya District were selected and 430 questionnaires were filled up by random-selected households of these nine neighborhoods. The questionnaires content was almost about inhabitants’ knowledge and their viewpoints on this issue. The data derived by the questionnaires were interpreted in SPSS and Microsoft Excel softwares. The findings were interpreted as a frequency distribution.

3. Results and Discussion

In this study, the knowledge of 430 households of Çankaya Districts from nine neighborhood (Table 1.) on recycling packaging wastes and the level of information about the activities carried out by local administrations was evaluated. In addition, the evaluation regarding the expectations on the accession of recycling containers in encouraging way during this process was also done reviewed.
Table 1. The number and percentage of households of Çankaya District interviewed

<table>
<thead>
<tr>
<th>Neighborhoods</th>
<th>Number</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seyranbağlar</td>
<td>50</td>
<td>11.6</td>
</tr>
<tr>
<td>Zafertepe</td>
<td>50</td>
<td>11.6</td>
</tr>
<tr>
<td>Yakupabdal</td>
<td>50</td>
<td>11.6</td>
</tr>
<tr>
<td>Çamlıtepe</td>
<td>50</td>
<td>11.6</td>
</tr>
<tr>
<td>Keklikpınar</td>
<td>50</td>
<td>11.6</td>
</tr>
<tr>
<td>Maltepe</td>
<td>50</td>
<td>11.6</td>
</tr>
<tr>
<td>Çayyolu</td>
<td>50</td>
<td>11.6</td>
</tr>
<tr>
<td>Yukarı Bahçelievler</td>
<td>50</td>
<td>11.6</td>
</tr>
<tr>
<td>Gaziosmanpaşa</td>
<td>25</td>
<td>5.8</td>
</tr>
<tr>
<td>Çukurambur</td>
<td>5</td>
<td>1.2</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>430</strong></td>
<td><strong>100.0</strong></td>
</tr>
</tbody>
</table>

In this survey, it was asked to the participants whether they had any knowledge about recycling of packaging wastes. The result of it revealed that more than 67% of households had information about the recycling process.

Table 2. Knowledge of households about recycling process

<table>
<thead>
<tr>
<th>Do you have knowledge about recycle ?</th>
<th>Number</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yes</td>
<td>291</td>
<td>67.7</td>
</tr>
<tr>
<td>No</td>
<td>139</td>
<td>32.3</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>430</strong></td>
<td><strong>100.0</strong></td>
</tr>
</tbody>
</table>

Furthermore, the source of this knowledge was evaluated. The results indicated that approximately 63% of the participants had knowledge from television programmes. The source of family and friends were ranked number two.

Table 3. Source of knowledge of households about recycling process

<table>
<thead>
<tr>
<th>Source of Knowledge</th>
<th>Number</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Textbooks</td>
<td>37</td>
<td>12.7</td>
</tr>
<tr>
<td>Family/friends</td>
<td>140</td>
<td>48.1</td>
</tr>
<tr>
<td>Periodical/newspaper</td>
<td>111</td>
<td>38.1</td>
</tr>
<tr>
<td>Television programmes</td>
<td>183</td>
<td>62.9</td>
</tr>
<tr>
<td>Internet</td>
<td>71</td>
<td>24.4</td>
</tr>
<tr>
<td>Municipality posters and brochures</td>
<td>40</td>
<td>13.7</td>
</tr>
<tr>
<td>No idea</td>
<td>1</td>
<td>0.3</td>
</tr>
<tr>
<td>Other sources</td>
<td>15</td>
<td>5.2</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>291</strong></td>
<td><strong>100.0</strong></td>
</tr>
</tbody>
</table>

However, the local administrations were found to not be enough affective in providing consciousness about the recycling.

Physical analysis and studying the composition of packaging waste in Turkey indicates that there are many types of wastes among the recyclable and energy recoverable materials such as paper, board, plastic, glass, metal and organic compounds in the mixture of waste. Recycling and the waste processes are so much effective in municipal waste managing which is really new issue in Turkey. The present activities of recycling system in performing the main projects were not successful because the absence of close attention from source seperation projects and lack of suitable support from public participation.

Performing the source separating system requires the people cooperation and public participation as well. Therefore a continuous public training programs through media centers
and persuading the executive organization to cooperate with municipalities are the most important elements for a successful achievement of this process. These achievements could also be drawn the attention of majority of experts and city managers as well.

References

TUIK, 2015. Turkish Statistical Institute, Population censusus.
Removal Efficiencies and Electricity Consumed of Pharmaceuticals by Electrocoagulation and UV Processes

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Keywords: Pharmaceuticals, micropollutants, UV, wastewater.

Abstract

In the last years, pharmaceuticals in the water cycle have taken attention as emerging contaminants. In this study, elimination of micropollutants in the effluents of an urban wastewater treatment plant (WWTP) using UV – UV/H₂O₂ treatment and electrocoagulation (EC) were investigated. For this purpose elimination rate and energy consumption of, N4-Acetyl-sulfamethoxazol (AcSmx), 1H-Benzotriazol (Benz), Carbamazepin (Cbo), Ciprofloxacin (Cipro), Clarithromycin (Cla), Diclofenac (Dic), Metoprolol (Met), Sulfamethoxazole (Smx) and Tramadol (Tram) were compared.

Results showed that all pharmaceuticals could be removed by more than 88% using UV and UV/H₂O₂ processes. On the other hand elimination rates of electrocoagulation are above 80%. Furthermore; electrocoagulation using iron electrodes are effective for the removal of pharmaceuticals and electricity consumed are lower than the UV process.

1. Introduction

Pharmaceuticals have been used throughout the world and compose a large group of human and veterinary medicinal compounds (Klavarioti et al. 2009). Micropollutants like pharmaceuticals and personal care products are detected in surface waters. (Fick et al., 2009; Tambosi et al., 2010; Richard et al., 2014; Wols et al., 2015). The main route of the pharmaceuticals in the surface waters are wastewaters and wastewater treatment plants (WWTPs) (Pereira et al., 2016; Teixeira et al., 2016; Nielsen and Bandosz, 2016). Pharmaceuticals have been detected in the aquatic environment from the range of μg L⁻¹ to ng L⁻¹ (Bayen et al., 2014; Corcoran et al., 2010; Monteiro and Boxall 2010).

A lot of research results, shows that conventional wastewater treatment technologies are ineffective in removing these compounds (Ternes et al., 2002; Janzen et al., 2011, Bergmann et al., 2011). These WWTP effluent can be treated with advanced oxidation processes (AOPs) to degrade the pharmaceuticals compounds (Canonica et al., 2008; Tuerk et al., 2010; Challis et al., 2014; Rosario-Ortiz et al., 2010). One of the effective advanced oxidation method is UV degradation (He et al., 2016; Stefan and Williamson, 2004). UV and H₂O₂ (UV/H₂O₂) effectively degrade many organic pollutants with creating typically hydroxyl radicals (•OH) (Goldstein et al. 2007; Vilhunnen et al., 2010).
Electrocoagulation (EC) is an alternative process to remove organic pollutants from waters and wastewaters (Barışçı et al., 2015; Tian et al., 2016). Aluminum and iron are mostly used as electrodes, because these are cheap, easily found and effective materials. (İrdemez et al., 2006; Chen et al., 2000).

The aim of this study is to compare elimination rates and energy requirements of the selected pharmaceuticals using UV and electrocoagulation processes.

2. Material Methods

Chemicals
High-purity deionized water (pure water) was produced by an Elix 10 – Milli-Q Plus water purification system (Millipore, Eschborn, Germany). Acetonitrile and formic acid were purchased from Merck (HPLC gradient grade, Darmstadt, Germany). The concentrations of the nine substances (AcSmx, Benz, Cbz, Cipro, Cla, Dic, Met, Smx, Tram) were 100 ng mL⁻¹ and the pH ranged from 7.4 to 8.

HPLC-MS/MS analysis
Samples were analyzed by HPLC-MS/MS. The MS detection was performed on a Q Trap 4500 (AB SCIEX, Germany). The Q Trap 4500 is connected to a 1100 HPLC system (Agilent Technologies, Germany). The chromatographic separation was performed on a 50 x 2 mm Chromolith® Fast Gradient RP 18e HPLC column (Merck, Germany) at 40 °C. The mobile phase consisted of 0.1% formic acid in water (v/v) (mobile phase A) and 0.1% formic acid in acetonitrile (v/v) (mobile phase B).

UV – UV/H₂O₂ Experiments
UV experiments were carried out with a 800 ml sample using an LP (low pressure) UV lamp with emission radiation range at 254 nm and with the addition of 1 gH₂O₂ L⁻¹.

Electrocoagulation Experiments
EC experiments were carried out with a 800 ml sample using aluminum and iron electrodes (EA-PS 3032-20B laboratory power supply). Active surface area of the electrodes was 35 cm². The solution was stirred with a magnetic stirrer at a speed of 100 RPM. The samples were taken at the different times from the EC reactor.

Figure 1. Electrocoagulation Process.
3. Results and Discussion

Elimination rates of the selected pharmaceuticals using UV oxidation and the experiment with the addition of 1 g H₂O₂ L⁻¹ are shown in Figure 2. It is understood that 360 minutes were required without addition H₂O₂ to sufficient removal of all pharmaceuticals. With the addition of 1 g L⁻¹ H₂O₂ the effective removal efficiency (> 98%) for all selective pharmaceuticals was reached in 20 minutes.

![Figure 2](image)

Alternatively, electrocoagulation experiments using aluminum electrodes were tested with 0.1 A and 10V, 0.1 A 10V with addition H₂O₂ and 0.2 A 25V with addition H₂O₂. As can be seen in figure 3, at the end of 120 minutes and 360 minutes it wasn’t an effective elimination expect Cipro and Cla.

![Figure 3](image)

The highest removal efficiency was reached using iron electrodes (15V and 0.1A) at the end of two hours. The results are shown in the figure 4.
In this study elimination rate and energy consumptions of the UV and electrocoagulation processes were compared using 9 pharmaceuticals. UV have been very effectively degrade all of the 9 pharmaceuticals with addition H\textsubscript{2}O\textsubscript{2} in 20 minutes (Figure 2.). Energy consumption of the UV - lamp is 15Wh\textsuperscript{-1} and for 20 minutes total energy consumption is 5W. Electrocoagulation with aluminum electrodes (10V and 0.1A) have been a degradation sufficiently only for Cipro without H\textsubscript{2}O\textsubscript{2} addition and for Cipro and Cla elimination rates are 93 % and 99 % respectively in 360 minutes with H\textsubscript{2}O\textsubscript{2} (1 gL\textsuperscript{-1}) addition (Figure 3.). Energy consumption is 10 W/h and for 3 hours requires 30 W total energy consumption. This situation shows that aluminum electrodes needs 6 times more energy than UV-lamp and can’t efficiently eliminates the selected pharmaceuticals except cipro and cla. Electrocoagulation using iron electrodes (15V and 0.1A) are effectively with addition H\textsubscript{2}O\textsubscript{2} for the removal of all selected pharmaceuticals, elimination rates between 76 – 99 % (Figure 4.). The energy consumption is 1.5 W/h and the end of 2 hours requires 3 W total energies. This energy consumption is less than UV processes (5W).

As a result; electrocoagulation using iron electrodes are effective for the removal of pharmaceuticals and energy requirements are lower than the UV process.

**Acknowledgement**

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**References**


Evaluation of Estrogenic Hormones in Water Reservoirs and Municipality Treatment Plants in Istanbul

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Keywords: endocrine disrupters, 17β-estradiol, estrone, hormone, waste water

Nowadays, treatment plants have been increasing due to the advancing technology and industrialization throughout Turkey and the world. This situation brings along the requirement to analyze the features of the waste water of treatment plants in a more detailed way. In recent years, it has been remarkable to see studies conducted on endocrine disrupting substances in waste waters and the effects of these substances on environment and public health. Being one of the estrogenic hormones, which are endocrine disrupting substances and found naturally in organisms, 17β-estradiol and estrone are highly important for ecological balance.

This study investigates the endocrine disrupting substances found in effluent of water treatment plants in large amounts following the determination of the current situation of 17β-estradiol and estrone.

1. Introduction

Endocrine-disrupting substances alter the function of the endocrine system and, eventually, in a healthy organism, or its progeny cause adverse health effects, which is defined as received from outside agents or compounds (Goldman et al. 2000).

Scientists have reported that, endocrine disrupting substances replicate hormones, inhibit or increase the hormone facilities and may have fatal effects on human and animal uriner systems (Fox, 2004; Zhaoin and Jianying, 2008).

It is well known that some pharmaceutical substances have endocrine disrupting effects. Moreover, some natural originated estrogen sources (estrone (E1), 17β-estradiol (E2), estriol (E3), (phytoestrogens)) and many synthetic estrogen compounds (alkylphenol, pesticide, polichlorinebiphenol, phthalates, bisphenol A, 17α-ethinylestradiol (EE2), etc.) have been reported to have estrogen-like effects. The most effective of the natural estrogen are reported to be 17β-estradiol and estrone (Suzuki and Maruyama 2006).

Endocrine-disrupting hormones found in surface water have a disruptive effect on the reproduction system by limiting the effect of reproduction, so that the feminisation of male fish, a decrease in ovulation number in female fish and genetic anomalies in microorganisms are some of the threats in aquatic environment (Belfroid et al. 1999). In particular, the endocrine disrupting hormone levels are increasing much more than influent of plant according to effluent which accumulates in the treatment plant sludge, so it enters the food chain by mixing soil with composted sludge. Furthermore, testicular cancer, puberty, female reproductive system disorders, low sperm quality are the result of exposure to estrogen in the fetal and neonatal period (Weber et al. 2002).
Hormones are transported to the natural environment directly (effluent water of treatment plants) or indirectly (agricultural originated surface waters). The main source of the hormones in the aquatic environment are via human and animal excretion system (De Mes et al. 2005; Jobling et al. 2006). From the natural estrogenic hormones estrone (E1), 17β-estradiol (E2) and estriol (E3) are found in humans in cholesterol. E1 is the dominant hormone in women in menopause. E2 is the most active female hormone in pre-menopausal periods and the highest estrogenic potential. E3 metabolism originates from E1 and E2 hormones (Mückter 2006).

Figure 1 shows the progress of synthetic hormones from excretion system of human to treatment plant influent. Both treatment sludge and effluent of plant plays a great role in the distribution of these hormones to the environment (Hamid and Eskicioglu 2012).

![Figure 1. Distribution of hormones to the environment.](image)

### 2. Material Methods

Determination of natural estrogenic hormone of 17β-estradiol and estrone was measured in 16 different treatment plants and 4 different water reservoirs located in Istanbul (Figure 2). Samples were bottled in opaque brown glass sampling bottles and were stored at +4 °C according to storage conditions determined in Standard Methods. Of these facilities; Buyukcekmece Lake, Terkos Lake, Ömerli and Alibey dams for reservoirs; Baltalimanı, Buyukcekmece, Yenikapi, Kucukcekmece, Kadikoy, Uskudar and Kucuksu wastewater pre-treatment; Bahcesehir and Tuzla conventional classical activated sludge treatment; Atakoy, Pasakoy and Terkos advanced biological wastewater treatment; Kagithane, Ikitelli, Buyukcekmece and Omerli operate as water treatment plants.

Therefore, in this study 17β-estradiol and estrone hormones were selected and samples were taken from municipal water and wastewater treatment plants in Istanbul and determined by ELISA (enzyme-linked immuno-sorbent assay) microplate reader at a wavelength of 450 nm using ELISA kits.
In this study, DRG-diagnostics kits were used for 17β-estradiol and Dia-Metra brand ELISA kits were used for measuring estrone concentrations. Values were calculated by DNM-9602 Perlong ELISA microplate reader and controlled by double check system.

3. Results and Discussion

Scope of the study: samples were taken from influence and effluent of drinking water treatments, water reservoirs, water dams and waste water treatment plants in Istanbul and the levels of 17β-estradiol and estrone hormones were determined in Table 1.

<table>
<thead>
<tr>
<th>Treatment Plant</th>
<th>Concentration (ng/L)</th>
<th>Removal (%)</th>
<th>Concentration (ng/L)</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inlet</td>
<td>Effluent</td>
<td>Inlet</td>
<td>Effluent</td>
</tr>
<tr>
<td>Baltalimanı</td>
<td>147</td>
<td>135</td>
<td>8</td>
<td>127</td>
</tr>
<tr>
<td>Büyükçekmece</td>
<td>215</td>
<td>187</td>
<td>13</td>
<td>137</td>
</tr>
<tr>
<td>Yenikapı</td>
<td>382</td>
<td>336</td>
<td>12</td>
<td>187</td>
</tr>
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<td>Kadıköy</td>
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<td>-</td>
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<td>Üsküdar</td>
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<td>82</td>
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<td>Ataköy</td>
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<td>30</td>
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</tr>
<tr>
<td>Bahçeşehir</td>
<td>263</td>
<td>166</td>
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<td>Terkos</td>
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<tr>
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<td>206</td>
<td>163</td>
<td>21</td>
<td>161</td>
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<tr>
<td>Büyükçekmece Lake</td>
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<td></td>
</tr>
<tr>
<td>Terkos Lake</td>
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<td>&lt;1</td>
</tr>
<tr>
<td>Ömerli Reservoir</td>
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<td></td>
</tr>
<tr>
<td>Alibey Reservoir</td>
<td>42</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

17β-estradiol concentrations in drinking water reservoirs was measured at 42 to 53 ng/L. High concentrations of 17β-estradiol in the watershed means that it is not well preserved. These hormone concentrations have no removal capacity in treatment plant effluent compared to influence.
As shown in drinking water treatment plants influence values of 17β-estradiol range from between 44 ng/L and 55 ng/L, where the effluent values 37 ng/L and 50 ng/L. It can be understood that pre-treatment plants have no removal capacity using today’s technology. These values range from between 140-382 ng/L influence in plants whereas the effluent ranges between 126-336 ng/L. Influence of biological wastewater treatment plant were between 81-267 ng/L, effluent of plant was 49-185 ng/L.

Estrone levels range between 48-187 ng/L at pre-treatment plants, 31-180 ng/L at treatment plant effluent and for biological treatment plants ranges were between influence and effluent, 80-177 ng/L and 58-125 ng/L, respectively.

Acknowledgement
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References
Elimination of Pharmaceutical Residues in Municipal Wastewater Using Advanced UV Irradiation Technology

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Keywords: Pharmaceuticals, micropollutants, UV, wastewater.

Abstract

Waste water discharges are an important input source for micropollutants like pharmaceuticals & personal care products (PCPP) and endocrine disrupting compounds (EDCs) for surface waters. Pharmaceuticals are being detected continuously around the world in waste water treatment plant (WWTP) effluents and the amount of organic micropollutants detected in surface waters increases steadily.

The aim of this work is the reduction of pharmaceuticals in a plot scale waste water treatment plant, based on UV- or UV/H₂O₂ oxidation processes. In this study the selected parameters Carbamazepin, Ciprofloxacin, Diclofenac, Metoprolol and Sulfamethoxazole were investigated.

1. Introduction

Major sources of micropollutants are households and hospitals. The aquatic environment is the most affected environment of pharmaceuticals which are consumed by humans and are entering the aquatic environment via urine, faeces and households. Several prescription medicaments, such as diclofenac, carbamazepine or Sulfamethoxazole have been found in surface, ground and drinking waters in concentration ranges from ng/L up to some μg/L.

During the discussion of the EU water framework directive (WFD), new priority substances on annex X and environmental quality standards (EQS) the European Commission established a watch list new emerging contaminants (EU, 2013). The prioritization and classification of environmental contaminants are currently a major issue in the scientific discussion. In a study of the Federal Environment Agency, an attempt was made to prioritize drugs in terms of their relevance in the aquatic environment. Carbamazepine, Diclofenac and Sulfamethoxazole were included on a list of priority substances, because of their relatively high environmental concentration (Bergmann et al., 2011). As basis for the evaluation of the ecotoxicological potential, measured or predicted environmental concentrations (MEC/PEC) and predicted no effect concentrations (PNEC) are used. Compounds with a MEC / PNEC ratio > 1 are of major concern. In Table 1, the no observed effect concentration (NOEC), MEC and PNEC values for some pharmaceuticals are listed. The MEC value is the maximum concentration in German surface waters. (Bergmann et al., 2011).
Table 1. Ecotoxicological data for selected drugs (Bergmann et al., 2011).

<table>
<thead>
<tr>
<th>Substance</th>
<th>NOEC [μg/L]</th>
<th>MECMAX [μg/L]</th>
<th>PNEC [μg/L]</th>
<th>MEC/PNEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbamazepine</td>
<td>25</td>
<td>6.1</td>
<td>2.5</td>
<td>2.4</td>
</tr>
<tr>
<td>Metoprolol</td>
<td>3,200</td>
<td>2.5</td>
<td>3.2</td>
<td>0.78</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>1.0</td>
<td>3.1</td>
<td>0.1</td>
<td>31</td>
</tr>
<tr>
<td>Sulfamethoxazol</td>
<td>5.9</td>
<td>1.13</td>
<td>0.59</td>
<td>1.9</td>
</tr>
</tbody>
</table>

With growing awareness of this problem a number of different concepts for the removal of micropollutants are investigated. These are essentially based on two different starting points. One is based on adsorption processes and the other on oxidation processes (Poyatos et al., 2009; Eggen et al., 2014). Advanced oxidation processes (AOPs) have been described as a useful instrument for the removal of micropollutants from waste waters (Tuerk et al., 2010). The oxidation products are also called transformation products and could be better biodegradable (Sires et al., 2014). Beside the direct reaction with ozone or UV light the fast reacting species of AOPs are hydroxyl radicals (•OH) (Von Gunten & Von Sonntag, 2012).

The degradation of micropollutants using UV / H₂O₂ oxidation process is based on a combination of oxidation by •OH radicals and direct photolysis. The oxidative degradation of contaminants with •OH radicals is most advanced oxidation processes in the foreground. This requires distinguishing the direct and indirect photolysis and oxidation by •OH radicals that are formed on the basis of a photo induced homolytic cleavage of H₂O₂ or H₂O (Plahuta et al., 2014). The aim of the oxidation of micropollutants is to generate smaller and possible more biodegradable molecules or to mineralize the micropollutant altogether (Keen et al., 2013).

### 2. Material Methods

The experiments were carried out at the Institut für Energie- und Umwelttechnik e. V. (IUTA, Institute of Energy and Environmental Technology) in Duisburg, Germany.

Samples are stored before enrichment at 4-8 °C. The SPE is carried out with 100 to 1000 mL waste water via Oasis HLB (Waters, City, Country) cartridges. For each series of samples one quality control (QC) sample and one blank sample are processed, in addition. For the QC sample 1 liter pure water is spiked with a standard mix (100 ng absolute) of the analyzed pharmaceuticals and the internal standard mix (100 ng absolute) is added. The blank sample is spiked only with the internal standard mix (100 ng absolute). The solid phase extraction procedure is carried out with an automatic SPE instrument (GX-281, Gilson, Limburg, Germany). The eluate (10 mL methanolic solution) is concentrated under a gentle nitrogen stream at 50 °C to dryness and redissolved with 1 mL of the starting LC-MS eluent (95% water and 5% acetonitrile containing each 0.1% formic acid), filtered through a syringe filter and filled into two HPLC vials. The second vial is used as a reference sample and stored for 3 months at -18 °C.

Samples were analyzed by HPLC-MS/MS. The MS detection was performed on a Q Trap 6500 (AB SCIEX, Germany). The Q Trap 6500 is connected to a 1100 HPLC system (Agilent Technologies, Germany). The chromatographic separation was performed on a 50 x 2 mm
Chromolith® Fast Gradient RP 18e HPLC column (Merck, Germany) at 40 °C. The mobile phase consisted of 0.1 % formic acid in water (v/v) (mobile phase A) and 0.1% formic acid in acetonitrile (v/v) (mobile phase B).

The UV and UV / H$_2$O$_2$ oxidation experiments were carried out at the WWTP Duisburg-Hochfeld with a continuous flow pilot scale. UV reactor (250 W, IBL Umwelt- und Biotechnik GmbH Deutschland) was used (Figure 1).

Experiments on UV and UV / H$_2$O$_2$ oxidation pilot scale at the WWTP Duisburg-Hochfeld were used to investigate the degradation behavior of persistent micropollutants in waste water treatment plant effluent. For this purpose, the removal efficiency has been carried out at different processing settings. One of these is the use of Quicksilver-Low Pressure (Hg-LP) lamp, setting 3 m$^3$/h flow rates and the addition of different concentrations of hydrogen peroxide as oxidation helper material (Table 3).

Before the start of each experiment, the UV Lamp had a lead time of at least 20 minutes. The scheme for the sampling for the individual experimental blocks the UV and UV / H$_2$O$_2$ elimination experiments are shown in table 2.

<table>
<thead>
<tr>
<th>1.</th>
<th>2.</th>
<th>3.</th>
<th>4.</th>
<th>5.</th>
<th>6.</th>
<th>7.</th>
<th>8.</th>
</tr>
</thead>
<tbody>
<tr>
<td>without treatment</td>
<td>only UV H$_2$O$_2$</td>
<td>UV + 25 mg H$_2$O$_2$</td>
<td>UV + 50 mg H$_2$O$_2$</td>
<td>UV + 100 mg H$_2$O$_2$</td>
<td>UV + 150 mg H$_2$O$_2$</td>
<td>UV + 200 mg H$_2$O$_2$</td>
<td>without treatment</td>
</tr>
</tbody>
</table>

3. **Results and Discussion**

The results of the work carried out for the detection and removal of pharmaceuticals are shown table 3 and 4.
Table 3: Concentrations of the investigated pharmaceuticals during the different experiments using an Hg-LP lamp at the WWTP-Hochfeld.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Carbamazepine c [ng/L]</th>
<th>Diclofenac c [ng/L]</th>
<th>Metoprolol c [ng/L]</th>
<th>Sulfamethoxazole c [ng/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>without treatment</td>
<td>3,200</td>
<td>11,000</td>
<td>5,400</td>
<td>700</td>
</tr>
<tr>
<td>only UV</td>
<td>3,200</td>
<td>8,100</td>
<td>5,000</td>
<td>600</td>
</tr>
<tr>
<td>UV + 25 mg H₂O₂/L</td>
<td>1,500</td>
<td>2,500</td>
<td>3,400</td>
<td>300</td>
</tr>
<tr>
<td>UV + 50 mg H₂O₂/L</td>
<td>1,300</td>
<td>3,100</td>
<td>4,000</td>
<td>300</td>
</tr>
<tr>
<td>UV + 100 mg H₂O₂/L</td>
<td>50</td>
<td>&lt;90</td>
<td>1,800</td>
<td>24</td>
</tr>
<tr>
<td>UV + 150 mg H₂O₂/L</td>
<td>17</td>
<td>&lt;90</td>
<td>450</td>
<td>&lt;2</td>
</tr>
<tr>
<td>UV + 200 mg H₂O₂/L</td>
<td>&lt;20</td>
<td>&lt;90</td>
<td>200</td>
<td>&lt;2</td>
</tr>
<tr>
<td>without treatment</td>
<td>3,300</td>
<td>11,000</td>
<td>5,300</td>
<td>600</td>
</tr>
</tbody>
</table>

Table 4: Elimination rate of pharmaceuticals using UV-LP Lamp in WWTP-Hochfeld.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Carbamazepine [%]</th>
<th>Diclofenac [%]</th>
<th>Metoprolol [%]</th>
<th>Sulfamethoxazole [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>only UV</td>
<td>0</td>
<td>26</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>UV + 25 mg H₂O₂/L</td>
<td>53</td>
<td>77</td>
<td>36</td>
<td>56</td>
</tr>
<tr>
<td>UV + 50 mg H₂O₂/L</td>
<td>59</td>
<td>72</td>
<td>26</td>
<td>56</td>
</tr>
<tr>
<td>UV + 100 mg H₂O₂/L</td>
<td>98</td>
<td>&gt;90</td>
<td>66</td>
<td>97</td>
</tr>
<tr>
<td>UV + 150 mg H₂O₂/L</td>
<td>99</td>
<td>&gt;90</td>
<td>92</td>
<td>&gt;99</td>
</tr>
<tr>
<td>UV + 200 mg H₂O₂/L</td>
<td>&gt;99</td>
<td>&gt;90</td>
<td>96</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

All measured concentrations (Table 3) were above the PNEC values and therefore the MEC / PNEC ratios were above 1. The degradation rates of the UV experiment without addition of H₂O₂ shows a maximum value of 26%. The UV-C wavelength of 254 nm is very well suited for the generation of •OH radicals by homolysis of H₂O₂. With the use of 100 mg H₂O₂ Carbamazepine, Diclofenac and Sulfamethoxazole removal could be increased to 90%. For Metoprolol with the use of 150 mg H₂O₂, removal was increased to 90%. On the other hand, to reach the MEC / PNEC ratio < 1 for Carbamazepine and Metoprolol only 25 mg/L H₂O₂, for Diclofenac 100 mg/L H₂O₂ and for Sulfamethoxazole only UV is enough.

References


Oxidation of Olive Oil Mill Wastewater for Conventional Treatment

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Keywords: Hydrogen peroxide-Oxidation-Olive oil mill-Oil removal

Abstract

Advanced oxidation process treatment method has been adapted to olive oil mill wastewater (OMW). Lots of olive oil mills have facilities in Aegean Region, Turkey. Wastewater, used in this study was collected from these fabrics founded in the cities of Izmir and Balıkesir. Because of the advanced and expensive treatment methods of this wastewater, makes regulations and limitations out of order. 95 -160°C temperature and up to 20 bar pressure were used with \( \text{H}_2\text{O}_2 \) and \( \text{Fe(SO)}_4 \) as an oxidant in wet oxidation method. Over 96% of oil & grease and 90% of Chemical Oxygen Demand (COD) removal was achieved using wet air oxidation in conditions with different amounts of \( \text{H}_2\text{O}_2 \) and \( \text{Fe(SO)}_4 \) in 60 minutes.

1. Introduction

Olive Mill Waste (OMW) is an effluent of the olive oil production process. It is known that OMW is a great problem in Mediterranean Countries, which farms olive and producing olive oil. Turkey is the 4th greatest producer in these countries which has a production about 1,46 million tons/year. Turkey has got 151 million olive trees for farming and was produced 1,464,000 tones olive in year 2008 (Güneysu, 2009).

In addition, characterization of olive oil mill wastewater determined as; Chemical Oxygen Demand (COD) 88 g/l, oil grease 9.2 g/l, total solids 10.2 g/l, suspended solids 5.02 g/l, orthophosphate 84 mg/l and pH 4.51.

Several treatment methods on OMW were tested, but most of them have negative usage for conventional treatment. Certain treatment methods that are used on olive oil mill wastewater are; diluting (Boari, 1990), settling (Al-Malah et.al., 2000), flotation (Curri et.al., 1980), centrifugation (Mitrakes et.al., 1996), filtration (Velioglu et.al., 1987; Bradley and Baruchello, 1980), thermal processes (Rozzi and Malpei, 1996), evaporation (Arjona et.al., 1999), pyrolysis (Di Giacomo et.al., 1989), neutralization (Mitrakes et.al., 1996), flocculation (Fiestas Ros De Ursinos and Borja-Padilla, 1992), chemical oxidation processes (Massignan et.al., 1988), advanced oxidation processes (Legrini et.al., 1993), fenton processes (Sun et.al., 2007), electrodcoagulation (Gotsi et.al., 2005), aerobic and anaerobic treatment processes (Borja et.al., 1996).

The wet-oxidation process increases the influence of hydrogen peroxide by high temperature and pressure. Simply, photolysis reactions of \( \text{H}_2\text{O}_2 \) and kinetics are given below;

**Starter:**

\[
\text{H}_2\text{O}_2 \stackrel{hv}{\longrightarrow} 2 \cdot \text{OH}
\]  

(1)

**Process:**

\[
\text{H}_2\text{O}_2 + \text{HO} \cdot \stackrel{k_2}{\longrightarrow} \text{HO}_2 \cdot + \text{H}_2\text{O}
\]

\[
k_2=2.7 \times 10^7 \text{M}^{-1}\text{s}^{-1}
\]  

200
H$_2$O$_2$ + HO• $\xrightarrow{k_3}$ HO• + H$_2$O + O$_2$  \hspace{1cm} k_3 = 3,7 M$^{-1}$s$^{-1}$ \hspace{3cm} (3)  

**Termination;**
HO• + HO• $\xrightarrow{k_4}$ H$_2$O$_2$  \hspace{1cm} k_4 = 1,1.10^{10} M^{-1}s^{-1} \hspace{3cm} (4)  
HO$_2$• + HO• $\xrightarrow{k_5}$ H$_2$O + O$_2$  \hspace{1cm} k_5 = 1,2.10^7 M^{-1}s^{-1} \hspace{3cm} (5)  
HO• + HO$_2$• $\xrightarrow{k_6}$ H$_2$O + O$_2$  \hspace{1cm} k_6 = 7,5.10^9 M^{-1}s^{-1} \hspace{3cm} (6)  

**Oxidation;**
Waste + HO• $\xrightarrow{}$ Products (CO$_2$ + H$_2$O + HO$_2$• + inorganic compounds) \hspace{3cm} (7)

1, 2 and 4$^{th}$ reactions are identified as hydroxyl radical formations (Lee et.al., 2004). In this study, 5 – 20% ratio of hydrogen peroxide was mixed with 100 ml of OMW and react at 950 C temperature, 10 bar pressure by 1 hour.

## 2. Materials Methods  

### 2.1. OMW Samples  
The samples were quickly analysed and stored at +4$^0$C.

### 2.2. Analytical Methods  
The analyses were carried out by the following methods (APHA-AWWA-WEF, 2001). Total solids (APHA-AWWA-WEF, 2001), suspended solids (APHA-AWWA-WEF, 2001), volatile solids (APHA-AWWA-WEF, 2001), COD (APHA-AWWA-WEF, 2001), oil grease (APHA-AWWA-WEF, 2001), phosphorus (APHA-AWWA-WEF, 2001), temperature (APHA-AWWA-WEF, 2001), and pH.

### 2.3. Wet Peroxidation Reactor  
The reactor was designed for working high temperature and pressure safely. It is constructed from stainless steel and works up to 300 bar pressure perfectly. Furthermore, the oxidizing agent we used in this study doesn’t harmful to the reactor. The reactor was equipped as a gas inlet valve for the increase the pressure, a hole for to inject the oxidant agent addition and a safety pressure valve to prevent from the dangers of high pressure. Figure 1 shows the schematic drawing of the wet peroxidation reactor.
4. Results and Discussion

Turkey-Aegean Region OMW was selected for study and characterized (Table 1).

Table 1. Characterization of raw Olive Mill Waste

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Oxygen Demand, mg/L</td>
<td>88064</td>
</tr>
<tr>
<td>Oil&amp;grease, mg/L</td>
<td>9217</td>
</tr>
<tr>
<td>Suspended Solids, mg/L</td>
<td>5020</td>
</tr>
<tr>
<td>Total Solids, mg/L</td>
<td>10212</td>
</tr>
<tr>
<td>Volatile Suspended Solids, mg/L</td>
<td>4480</td>
</tr>
<tr>
<td>Phosphorus, mg/L</td>
<td>84</td>
</tr>
<tr>
<td>pH (T=20 °C)</td>
<td>4.51</td>
</tr>
</tbody>
</table>

As seen from Table 1 high content of COD and oil grease content makes the conventional treatment impossible.

Table 2. COD values after wet peroxidation

<table>
<thead>
<tr>
<th>Concentration</th>
<th>COD, mg/L [88064 mg/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0035 mol H$_2$O$_2$/100 ml</td>
<td>67193</td>
</tr>
<tr>
<td>0.014 mol H$_2$O$_2$/100 ml</td>
<td>60928</td>
</tr>
<tr>
<td>0.032 mol H$_2$O$_2$/100 ml</td>
<td>57330</td>
</tr>
<tr>
<td>0.056 mol H$_2$O$_2$/100 ml</td>
<td>45360</td>
</tr>
</tbody>
</table>

It has been obtained from the experiments’ oil – grease removal efficiency was about 97%, whereas COD removal efficiency was 48% of the wet peroxidation process with 0.056 mol H$_2$O$_2$/100 ml OMW. The removal of the oil – grease parameter was significant as the main
performance criteria in this study. Table 2 shows the COD removal by the hydrogen peroxide amount used in the process.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Oil grease,mg/L [9217 mg/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0035 mol H$_2$O$_2$/100 ml</td>
<td>1850</td>
</tr>
<tr>
<td>0.014 mol H$_2$O$_2$/100 ml</td>
<td>812</td>
</tr>
<tr>
<td>0.032 mol H$_2$O$_2$/100 ml</td>
<td>536</td>
</tr>
<tr>
<td>0.056 mol H$_2$O$_2$/100 ml</td>
<td>302</td>
</tr>
</tbody>
</table>

As mentioned in the Table 2 and 3 wet peroxidation conditions were determined as; 10 bar reactor pressure, 950 °C reaction temperature and 1 hour reaction time within the 0.0035, 0.014, 0.032 and 0.056 mol hydrogen peroxide addition to 100 ml of OMW.

![Removal diagram of COD and oil&grease](image)

Figure 2 indicates the removal of COD and oil&grease by wet peroxidation. Y-apsis of the diagram shows COD and oil&grease values as mg/l, whereas X-apsis shows the mole of hydrogen peroxide added to the reactor per 100 ml of wastewater.

5. Results and Discussion

With the aim of the increase, the efficiency with different oxidation experiments was tried out at a temperature of 950 °C, 10 bar nitrogen gas pressure and one hour reaction time. Table 2 and Table 3 states that the hydrogen peroxide added the raw OMW as an oxidant with the following values; 0.0035, 0.014, 0.032 and 0.056 mol and COD and oil&grease removal were calculated as 48.5% and 96.7% respectively.

The higher rate of hydrogen peroxide added to wastewater has the higher removal capacity on COD and oil&grease. We know from literature that to remove 1 g of COD, theoretically 0.0625 mol H$_2$O$_2$ is to be needed (Genç et.al., 2002). OMW used in this study was characterized as
204 mg/l COD value and as theoretically 5 moles of H2O2 are to be needed for oxidation. Optimum hydrogen peroxide dose, which was calculated from response surface methodology is less than the theoretical amount, this can be explained as increasing the oxidant efficiency by reaction temperature and pressure. Furthermore, removal ratio of oil&grease was calculated as 96.7%, but still 302 mg/l residual value couldn’t have removed so this value is too high to discharge according to Water Pollution and Control Regulations (http://www.cevreorman.gov.tr) and second treatment has to be done.

References


Using Wastes as Alternative Energy Sources in a Combustion Chamber: AKÇANSA Model

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Keywords: Waste-to-Energy, clinker production, waste management.

Abstract

In this study, cement production processes and waste management approach by waste-to energy application were discussed on a real system cement production company titled AKÇANSA Cement Ltd. in Istanbul.

During cement production, fossil fuels are consumed to provide the requirement of high heat for clinker production. Since energy demand has been getting more and more critical, organic wastes with high calorific value have been used in the last few years. Waste-to energy concept helps companies manage a wide variety types of waste produced by many different industries. This will also help prevent that amount of waste to be disposed in the landfill. Wastewater treatment sludge, waste tires, plastic wastes etc. are some types of wastes which are used to be burned in combustion chamber for heat production.

Fuel consumption to provide heat for clinker production (38\%) and need for electricity (21\%) are two main expenditures for cements companies. Hence, energy production from alternative sources is getting more important for each industry. AKÇANSA managed to save 310.000 tons of coal by recovering energy from 340.000 tonnes of waste between 2009-2013.

1. Introduction

The first stage in the production of cement is clinker production. The composition called raw meal forms when raw materials such as clinker, lime stone, marl and clay are homogenised. Clinker is produced by heating the raw material in rotary kilns using primary fuels such as coal, petroleum coke, lignite, natural gas and alternative fuels at 1400-1500 °C. The second stage is the stage where plaster and other materials (limestone, blast-furnace slag, volatile coal ash, natural pozzolana etc.) are added onto the clinker and grinded in grinders. Cement is produced by grinding all components in cement grinders slimly and homogeneously. Figure 1 shows the cement production flow diagram.
One of the most critical processes in cement production is clinker production. Rotary kilns are the reactors where all chemical transformations needed for clinker production take place. In heating process which is carried out in rotary kilns, it is critical to heat the kiln up to the desired level and to keep it stable throughout the reaction process. Clinker production in rotary kilns at high temperature is the most important process in terms of the product quality and the cost. It is highly important to keep the temperature at 1400-1500°C during the process of clinker production in rotary kilns. In this process, the raw meal is fed into graded pre-heating cyclones from silos in which it is homogenised. The materials coming via these cyclones lose their humidity and a portion of (40-50%) calcination reaction takes place when the raw meal contacts the hot gasses from the kiln. By adding calcinator to pre-heater towers, the calcination can be increased up to 95%. Heat consumption falls by 5-10% in calcinators in kilns with pre-calcinator and kiln capacity increases. When raw meal which underwent a portion of calcination reaction is fed into rotary kilns, the calcination reaction is completed. Clinker which is formed as a result of the reactions which take place in the sinter area (1250-1450°C) of the kiln (sintering and clinkerization reactions) is poured into the cooling area. The cooling can be carried out while being poured into the cooling area and with air blown by high-pressure fans in the cooling area or with cooling tubes. Then, the clinker which is cooled down to about 100°C is transferred into clinker stokehold. There are many articles in the literature on CO2 emissions, life-cycle analyses and the effect of cement production processes on global warming (Song et al., 2016; Ruan and Unluer, 2016; Wang et al., 2016). Many alternative and advanced technologies are being developed in our day to minimize its negative environmental effects and it is aimed to improve the said processes globally (Boldyryev et al., 2016; Chen et al., 2016; Stafford et al., 2016; Stafford et al., 2016).

In parallel with the increasing world population, the increasing need for infrastructure has shown itself in Turkey, too and Turkey became and is the country which produces the highest amount of cement in Europe since 2009 (CAR, 2012). According to 2013-statistics, the country producing the highest amount of cement in the world is the People’s Republic of China with its 2300 million-tons/year cement production. India produces 280 million-ton, USA produces 78 million-ton, Iran produces 75 million-ton of cement and Turkey ranks 5th with its 70 million-ton production. It ranks first in Europe. The Figure 2.9 below shows the development of cement production according to regions (Europe, America, Africa, Asia/Oceania and Commonwealth of Independent States). It is seen that the production increased most in Asia in recent years and that it is the region which produced highest amount in 2014. When countries which export cement are analysed, Turkey ranks 2nd with 739.6 billion USD according to 2013 data. The
The importation of cement in Turkey was realized with 13.3 million USD. In 2014, these values were 641 million USD and 14.3 million USD, respectively (CAR, 2014).

The cement sector is a sector in which there is a great amount of energy and cement production is a process which consumes high amount of energy. Energy consumption is 30% in cement grinding stage, 27% in raw material grinding stage, 4% in coal grinding stage, 3% in crushing stage, 5% during mining activities and 24% in clinker cooling stage. The percentages of energy consumption in the production process are given in Figure 2.

![Figure 2. Energy consumption due to cement production steps.](image-url)

The primary fuels used in the cement sector are petroleum coke and lignite. Turkey imports these fuels which have a high calorific value from far regions such as Asia and America. Alternative fuels are also used to generate the required heat in the cement production since the fossil fuels which are used as primary fuel; can get more expensive, increase the dependency on foreign sources, have the risk of being depleted and create the risk of climate change due to high emission values. Industrial and domestic wastes are transformed into alternative fuel within the scope of the permissions/licences granted by the Ministry of Environment and Urbanisation (MEU) in 35 of 50 integrated cement factory which are active in our country.

The effects of the fuels on the process, product features and air quality need to be at an acceptable level in the use of the alternative wastes in cement sector. The wastes to be used as fuel need to meet the waste-acceptance criteria of the factory. The other criteria to take into account is the calorific value of the alternative fuels. Since the calorific value of the wastes change according to the quality of the material, the values given in Table 1 are accepted as average values.
Table 1. Average calorific value of some alternative fuels.

<table>
<thead>
<tr>
<th>Alternative Fuel</th>
<th>Average Calorific Value (kcal/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste oils</td>
<td>9000</td>
</tr>
<tr>
<td>Solvents</td>
<td>7500</td>
</tr>
<tr>
<td>Worn out tires</td>
<td>5500</td>
</tr>
<tr>
<td>Industrial plastic</td>
<td>5000</td>
</tr>
<tr>
<td>Plant skin</td>
<td>4760</td>
</tr>
<tr>
<td>Oily contaminated wastes</td>
<td>3500</td>
</tr>
<tr>
<td>Treatment sludge</td>
<td>3000</td>
</tr>
<tr>
<td>Contaminated wastes</td>
<td>3000</td>
</tr>
<tr>
<td>Refuse-derived fuel (RDF)</td>
<td>2800</td>
</tr>
</tbody>
</table>

The use of wastes in cement factories as alternative fuel is not called disposal but recovery. When the waste management hierarchy is analyzed within the scope of waste management, the combustion of wastes in cement facilities is called recovery, therefore they come before burning facilities. Besides the advantages of alternative fuel use, there are some disadvantages, too. In order to facilitate the recovery of any waste to be used in cement sector, high infrastructure investments are needed. There are investment and operating costs arising from the use of alternative fuels. Investment costs are related to storing, laboratories, continuous measurement devices, waste preparation, drying and installation of feeding systems. Operating costs are related to getting a licence, operating the continuous measurement devices (calibration, annual tests etc.), periodical emission measurements, additional staff costs and maintenance expenses arising from the alternative fuels. There are also a set of challenges in cement production process. Fuels with especially high amount of chloride and sulphur can cause congestions in cyclones and undesired halts in the rotating kilns. Therefore, some works and reformative methods are being studied for ensuring a sustainable production in factories.

When the alternative fuel use projection is analyzed, the alternative fuel use rate which was 5% in developing countries and 16% in developed countries in 2006 is expected to increase to 10-20% and 40% in 2030, respectively. While no change is foreseen in the developed countries in the time period up to 2050, it is predicted that this value will be 25-35% in developing countries.

2. Material and Methods

The method used in the study is based on the process follow-up and analysis. The work flow of a major cement production company active in our country was analysed. The types of fuels used to generate the calorific energy needed in the clinker production process were determined and their in-process uses were researched with the aim of energy recovery of waste materials. The internal inspection data of the firm (Akçansa Sustainability Reports) were used, a situation assessment was conducted, and results were compiled and presented.

3. Results and Discussion

There are 3 actively used raw material crusher in the factory, the crushed materials are analysed online with the radioactive online analyser and are stored in 50,000-ton circular stokehold. The coal which is obtained in crushed from is kept in a coal stokehold of 9,000 ton capacity with a long shape. There are 2 ball grinders and 2 vertical grinders within the facility for raw meal grinding stages and one of the vertical grinders can also be used for additional grinding in cement production. The quality is simultaneously analysed with the radioactive online analyser.
system in raw meal grinder 2. The clinker produced in rotating kilns are stored in 60,000-ton and 35,000-ton clinker stokeholds. Cement grinding processes are carried out in 4 grinders and cement grinder 1 has the rollerpress system. New generation separator system investments have recently been made for cement grinder 1 and 2. 10 cement silos within the factory make it possible for 27,000-ton cement to be stocked. The production capacity of the rotating kilns in which clinker is produced is 1325 tons/day, 2850 tons/day and 1625 tons/day, respectively.

Hazardous wastes are sent to the third facility and accepted by the facility manager. Safe wastes are accepted by a contracted recovery company. Oil wastes are sent to the 1st Facility and accepted by the facility manager.

The wastes that can be accepted by the Akçansa Büyükçekmece factory are brought to the factory in line with the regulations and are shaped in a way to be used in production. There are several procedures for a waste to be accepted to the factory. First, a waste study is conducted. Samples are requested from the firm with the waste. The information form containing info such as waste type, which industry or process the waste is produced from, waste amount, firm name and firm representative is given to the laboratory and the sample is analysed. After the analysis, the process managers and laboratory managers gather together and an evaluation is conducted, and if approved, the relevant firm is contacted and a contract is signed. As a basic rule, the wastes accepted as alternative fuel, calorific value of the organic part and material value of mineral part must be present on the added-value in rotating kilns.

The average alternative fuel use rates of Akçansa Cement Factories (Büyükçekmece, Çanakkale, Ladik) increased as follows: 2.9% in 2009, 4% in 2010, 4.6% in 2011, 5.2% in 2012 and 6.7% in 2013. On the other hand, these rate were 9%, 11.7%, 12.7% and 14.6% respectively and increased to 14.8% with 79,221-ton alternative fuel use in 2013.

In the facility, domestic wastes, garbage and industrial plastic wastes were burned in a calcinator designed separately from the kiln, as a first-time practice in the world. In this way, the imported fossil fuel amount was reduced. In this process, the capacity of the factory to burn wastes significantly increased. The capacity in the other two kilns which was 4 tons/hour was increased to 10 tons/hour with a 6 tons/hour additional doser. As a result of this, 47,500-ton domestic waste was disposed of. In the 5 years between 2009-2013, 340,000-ton waste was utilized as alternative fuel and in this way, 310,000-ton domestic coal was saved (Akçansa Sustainability Report, 2013).

The calorific energy required in the rotating kilns are met with coal, petroleum coke, natural gas and alternative fuels. Year-specific use rates of the fuels used in cement production in Akçansa Büyükçekmece Factory are given in Table 2. Alternative fuel use rate which increased since 2009, decreased in 2015 and fell to 9.06%, the coal use rate which had recently been decreasing, on the other hand, increased.

<table>
<thead>
<tr>
<th>FUEL TYPE</th>
<th>2013</th>
<th>2014</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>27.3</td>
<td>25.7</td>
<td>35.33</td>
</tr>
<tr>
<td>Petroleum Coke</td>
<td>57.6</td>
<td>58.5</td>
<td>55.4</td>
</tr>
<tr>
<td>Natural Gas</td>
<td>0.4</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Alternative Fuel</td>
<td>14.7</td>
<td>15.5</td>
<td>9.06</td>
</tr>
</tbody>
</table>
While it is ensured that the natural resources are preserved and the amount of carbon dioxide emitted into the atmosphere is significantly reduced by burning wastes that can be used as alternative fuel in rotating kilns with calorific processes at high temperatures in cement factories, the process also provides a solution for waste disposal which is a major problem. The organic materials within the wastes are completely removed with calorific processes and oxidizing environment in the high-temperature kilns. Inorganic materials, on the other hand, takes the place of the raw materials and become a part of the cement. The use of alternative fuels in cement factories reduces the need for burning facilities and prevents more emission and ash formation in burning facilities. When cost items of the cement sector are analysed, fuels (38%) and electricity (21.1%) have the biggest shares. The trend of using alternative fuels in parallel with the determination to find a solution to environmental problems and the high prices of primary fuels has been recently increasing in our country. The studies conducted on the energy efficiency of cement factories show that a significant amount of energy can be saved.

References


Recycle of Construction and Demolition Wastes: An Overview of Potential Uses in Geotechnical Applications

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Keywords: Construction and demolition wastes, recycling, beneficial usage, geotechnical applications

Abstract

The recycled construction and demolition waste (CDW) materials such as masonry and concrete may be used in various geotechnical applications. In this study, the recycle of CDWs was reviewed, and the potential uses of recycled CDW materials in geotechnical applications were discussed considering studies reported in the literature in the last decade.

1. Introduction

It is well known that the construction industry, which consumes a huge amount of natural resources and generates large quantities of construction and demolition waste (CDW), is one of the largest sectors of the world economy (Poon, 2007). Construction, renovation and demolition activities concerning buildings, utilities, structures and roads do not only result in huge volumes of CDW, but also have to be disposed of and managed, leading to serious financial and environmental implications (Bernardo et al., 2016). Construction industry is responsible for 50% of the worldwide consumption of natural resources (Oyedelea et al., 2014; Cristelo et al., 2016), and generates a large portion of waste to landfill (Oyedelea et al., 2014).

According to the European Waste Catalogue (Commission Decision, 2000/532/EC), CDWs can be composed of concrete, bricks, tiles and ceramics; wood, glass and plastic; bituminous mixtures, coal tar and tarred products; metals; soil (including soil excavated from contaminated sites), stones and dredging spoil; insulation materials and asbestos-containing construction materials; gypsum-based construction material; and other construction and demolition materials. CDW is generally defined as a mixture of inert and non-inert materials arising from construction, excavation, renovation, demolition, roadwork and other construction-related activities. The inert materials are divided into two groups as hard and soft inert materials. Hard inert materials consist of rocks and broken concrete, whereas soft inert materials consist of soil, earth and slurry. The non-inert materials include wastes such as timber, plastics, metals and packaging wastes (Poon, 2007).

As stated by Vieira and Pereira, the full or partial replacement of soils and conventional aggregates by CDW materials can contribute significantly to the mitigation of environmental impacts induced by the construction industry, and thereby contribute to the reduction of our ecological footprint (Vieira and Pereira, 2015). In principle, all concrete and masonry waste can be recycled and reused (Kartam et al., 2004). Up to now, uses of CDW materials in geotechnical applications such as geosynthetic reinforced structures, roadway infrastructures, alternative pipe backfilling materials, landfill cover layer, vibro ground improvement processes, and gabion filling material was studied by various researchers (Yeung et al., 2006; Leite et al., 2011; Rahman et al., 2014; Arulrajah et al., 2014; Galvin et al., 2014; Vieira et al., 2015; Bhuiyan et
The objective of this paper is to review the recycle of CDWs. The main objective is to discuss the use of the recycled CDWs in geotechnical engineering applications. In the study, the overview of the recycle of CDWs was presented. The potential uses of recycled CDWs in geotechnical applications were reported considering studies reported in the literature in the last decade.

2. Construction and demolition wastes (CDWs)

2.1. Classification of CDW materials

CDWs can be classified into five categories depending on the nature of works: roadwork material, excavated soil, demolition waste, site clearance waste, and renovation waste (Poon et al., 2001).

There are two main kinds of building CDW: structure waste and finishing waste. Structure waste consists of concrete fragments, steel reinforcement, abandoned timber plates and pieces generated during the course of construction. Finishing waste is generated in the finishing stage of the building, and includes a wide range of waste materials such as household facilities like damaged bathtubs, washtubs and window frames; broken raw materials such as mosaic, tiles, ceramics, paints and plastering materials; and surplus cement mortar arising from screeding scatters over the floors inside the building. CDW mainly consists of inert materials like bricks, sand and concrete. The non-inert materials like metals, timber, paper, glass, plastics and other mixed materials make up the lesser percentages (Poon et al., 2001). In Fig. 1, the classification of recycled construction materials is given.

![Figure 1. Classification of recycled construction materials (Oyedelea et al., 2014).](image)

2.2. The recycle of CDW materials and their potential uses

The reduction of non-renewable natural resource extraction is a constant concern relating to the preservation of the environment, and encourages the use of recycled materials. In the recent years, environmental sustainability has demanded a decrease in the exploitation of non-renewable resources and a progressive increase in waste valorisation in diverse areas. The valorization of wastes in the construction industry is, therefore, a need and one way forward for sustainability (Vieira and Pereira, 2015).
CDWs are increasingly used as construction materials in engineering applications. Potential uses of recycled CDW are ground improvement, engineered fills, road construction, pipe bedding, drainage and backfill material, pavements, aggregates in concrete, production of cement blocks using powdered concrete, planting medium, and water bound layers (Arulrajah et al., 2014, Kartam et al., 2004). However, in order for the recycled materials to be marketed as a substitute for natural raw materials, it is necessary that the recycled materials satisfy the given technical specifications and be economically competitive (Kartam et al., 2004).

Various governments across the world, especially in the developed nations, are continuously setting targets towards reducing the environmental impacts as a result of their construction activities. Among these means of reducing environmental impacts due to construction activities are various government led campaign, legislation and initiatives such as the use of BREEAM and Code for Sustainable Homes (CfSH) for sustainable building appraisal, Site Waste Management Plan (SWMP), Aggregate Levy, and the imposition of landfill tax to discourage waste to landfill, and to promote materials re-use and recycling (Oyedelea et al., 2014).

2.3. Potential uses of recycled CDW in geotechnical applications

Worldwide, numerous studies have been conducted to evaluate the possibility of using recycled CDW (Arisha et al., 2016). In the light of recent studies reported in the literature in last decade, it can be seen that recycled CDW materials can be used in various geotechnical applications.

Yeung et al. (2006) investigated the possibility of the use of inert CWD materials for seawall foundation by a field-scale pilot test. The results indicated that the use of public fill materials for seawall and breakwater foundation construction does not only present a viable solution to recycle CDWs, but also an effective means to allocate sand fill resources.

Leite et al. (2011) carried out a study to evaluate the feasibility of using aggregate from recycled CDW in pavement applications. The laboratory test results showed that the recycled CDW aggregate may be utilized as coarse base and sub-base layer for low-volume roads. The results obtained in this research encouraged the use of recycled CDW aggregates as a viable alternative for road construction. It was concluded that the composition and the compaction effort are important factors in the physical and mechanical behavior of the recycled CDW aggregates.

Arulrajah et al. (2013) conducted a study on the geotechnical and geoenvironmental properties of various recycled CDWs (recycled concrete aggregate, crushed brick, reclaimed asphalt pavement, waste excavation rock, fine recycled glass and medium recycled glass) in pavement subbase applications. Test results suggested that the recycled concrete aggregate and waste rock were found to have geotechnical engineering properties equivalent or superior to that of typical quarry granular subbase materials. Crushed brick at the lower target moisture contents of 70% of the optimum moisture content was also found to meet the requirements of typical quarry granular subbase materials. They suggest that the properties of crushed brick, reclaimed asphalt pavement, and fine recycled glass, however, may be further enhanced with additives or mixed in blends with high quality aggregates to enable their usage in pavement subbases.

Rahman et al. (2014) studied the suitability of various recycled CDWs (crushed brick, recycled concrete aggregate and reclaimed asphalt pavement) as alternative pipe backfilling materials. The results obtained in this research showed that the traditional waste materials can be reused viably as alternate pipe backfilling materials.
Arulrajah et al. (2014) examined the physical properties and shear strength responses of various recycled CDWs (recycled concrete aggregate, crushed brick, reclaimed asphalt pavement, waste excavation rock, fine recycled glass and medium recycled glass) in unbound pavement base/subbase applications. The results demonstrated that recycled concrete aggregate, crushed brick and waste excavation rock in particular are found to also meet the physical and shear strength requirements for aggregates in pavement base/subbase applications.

Mohammadinia et al. (2015) carried out a study for the extensive laboratory evaluation of the use of various cement-treated CDWs in pavement base and subbase applications. This research study indicates that cement-treated CDWs (reclaimed asphalt pavement, recycled concrete aggregate and crushed brick) are viable alternative materials for cement-treated pavement base/subbase applications. The authors also revealed that their usage in pavement base/subbase applications would significantly lower the carbon footprint for future road constructions.

Vieira et al. (2015) discussed the effects produced by the recycled CDW on geosynthetic samples exhumed after 6 months of the embankment construction. They found that the results of tensile tests carried out on intact and exhumed specimens indicate that the effects of the CDW on the short-term load–strain behaviour of the geosynthetics depend on the structure and base polymer of the material. On the HDPE geogrid, the recycled CDW induced a small decrease on the geogrid tensile strength and the reduction of the geogrid tensile stiffness. The recycled CDW induced the reduction of the geocomposite tensile strength (16% on average) but the effect on the geocomposite tensile stiffness is not significant. The shape of the load–strain curves for intact and exhumed specimens are, on average, quite similar.

Bhuiyan et al. (2015) investigated the possibility of the application of recycled concrete aggregates as alternative granular infills in hollow segmental block systems. Test results showed that the angle of friction of the blocks infilled with the recycled aggregate is almost equal to those with the fresh aggregate. The results also indicated that the compressive strength of the source waste concretes has a little or no effect on the frictional performance of the recycled concrete aggregates used in facing units.

Rahman et al. (2015) assessed the suitability of crushed brick, recycled concrete aggregate and reclaimed asphalt pavement, which are recycled CDWs, in permeable pavement systems by considering geotechnical and hydraulic characteristics. The results indicated that, in terms of usage in permeable pavement filter layer, CDWs were found to have geotechnical and hydraulic properties equivalent or superior to that of typical quarry granular materials.

Cristello et al. (2016) examined the geotechnical and geoenvironmental assessment of recycled CDW for road embankments. Results showed that this particular CDW batch was environmentally sound, and in accordance with the limits imposed by the European Directive 2003/33/EC.

Cardoso et al. (2016) reviewed the literature related to the use of recycled aggregates from CDW in geotechnical applications. The results collected from the literature indicated that the performance of most recycled aggregates is comparable to that of natural aggregates and can be used in unbound pavement layers or in other applications requiring compaction.

Vieira et al. (2016) assessed the feasibility of using fine-grain recycled CDW as filling material of geosynthetic reinforced structures (GRS), appraising the physical, mechanical and environmental characterization of the CDW. The results demonstrated that even so, it is
possible to state that the use of recycled CDW as filling material of geosynthetic reinforced structures seems to be an auspicious solution, able to balance the environmental and economic demands of current societies.

Arisha et al. (2016) investigated the possibility of using as unbound granular materials of blends of CDWs with recycled clay masonry brick (RCM) in pavement. The results indicated that RCM materials (100%) as unbound granular materials failed to meet the requirements of Los Angeles abrasion test of 50% maximum as specified by the Egyptian Code of Practice. Repeated Load Triaxial Testing data showed that all CDW/RCM blends yielded high resilient moduli however, no significant variation in resilient moduli values were observed between the different CDW/RCM blends.

Vieira and Lurdes Lopes (2016) investigated the damage induced by recycled aggregates on the short-term tensile behaviour of a high-strength geotextile. The results obtained from the study showed that, as expected the degradation induced by the recycled CDW after 6 months of exposure is not very expressive. On the HDPE geogrid the recycled CDW induced a small decrease on the tensile strength and the reduction of the tensile stiffness modulus. The geocomposite experienced some reduction on the tensile strength (16% on average) but the effects on tensile stiffness and shape of the load–strain curves were not significant.

3. Conclusion

The results obtained by various researchers, which are mentioned above, showed that recycled CDWs can be used in the various geotechnical applications such as geosynthetic reinforced structures, roadway infrastructures, alternative pipe backfilling materials, and landfill cover layer. However, recycled CDW materials should be carefully controlled by various physical and geotechnical characterisation tests, before and after their application. It should be noted that physical and geotechnical characterisation tests such as particle size distribution and gradation, specific gravity, water absorption, Los Angeles abrasion, unconfined compression, direct shear and triaxial tests, California Bearing Ratio and modified Proctor compaction tests should be undertaken. Chemical properties should be determined, including organic content, pH, trace element or total concentration and leachate testing of the CDW materials.

References


Single and Binary Adsorption of Iron and Manganese Using Three Activated Pumice Composites

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Keywords: Pumice, iron, manganese, adsorption, single and binary systems, surface modification

Abstract

Adsorption performance of Fe and Mn using three different activated pumice composites at varying doses, pH, and initial metal conditions was investigated in the single and binary metal systems.

Adsorption performance of Fe was found to be higher than Mn adsorption at all adsorption conditions. Consequently, a 100\% Fe removal was observed while a 64\% of Mn removal was recorded. Adsorption efficiency of HCl and HNO\textsubscript{3} activated pumice composites were found to be close to each other that they were eventually higher than H\textsubscript{2}O\textsubscript{2} activated pumice results. Removal of Fe or Mn decreased to some extent in binary system compared to single system at all pumice composites.

In conclusion, adsorption of Fe and Mn using pumice composites is promising to yield low cost and effective to be comparable with other low cost adsorbents.

1. Introduction

Heavy metals are mainly non-biodegradable and tend to accumulate in living organisms, causing various diseases (Al-Anber et al., 2008). Iron (Fe) and Manganese (Mn) exist in the wastewater and Fe can cause anorexia, oligura and diphasic shock whereas Mn can effect nervous and endocrine systems (Al-Anber et al., 2008; Dawodu et al., 2014; Khobragade et al., 2014; Grygo-Szymanko et al., 2016). Furthermore, Fe and Mn commonly exist in the groundwater and potable water and they are not preferred due to the unpleasant taste, color and odor, turbidity (Al-Anber et al., 2008).

Adsorption is one of the most suitable and widely used methods for removal of metals due to the cost effective and easy operations (Bailey et al., 1999). Pumice is a low cost material and it has a large porous surface area. Researchs showed that most of the metals can successfully be adsorbed onto pumice and pumice composites (Çifçi and Meric, 2016).

Aim of this study is to evaluate the effect of the acid activation of the surface of pumice using HCl, HNO\textsubscript{3} and H\textsubscript{2}O\textsubscript{2} on the removal of Fe and Mn in the single and binary adsorption systems as the novelty part of this study. The effect of the amount of pumice, pH and initial Fe or Mn concentrations on the adsorption performance was investigated and langmuir isotherms of Fe and Mn in both adsorption systems were obtained at optimum process conditions.
2. Material Methods

2.1 Activation of Pumice

The pumice powder was obtained from Nevşehir (particle size 0-125 microns). Activation of pumice surface was made using $\text{H}_2\text{O}_2$ (P1), $\text{HNO}_3$ (P2) and $\text{HCl}$ (P3). First, 50 g pumice was added to 250 mL solution that was contained a volumetric ratio of 1:10 of P1, P2 and P3. Pumice was stirred in the solutions for 24 h and washed several times with distilled water and dried at 105°C for 24 h.

2.2 Adsorption Experiments

Adsorption experiments were performed in 100 mL flasks and shaked at 200 rpm speed for 24 h. Mn (20 mg/L) and Fe (20 mg/L) removal for single adsorption system and Fe-Mn (20 mg/L for Fe and 20 mg/L for Mn) for binary adsorption systems were evaluated in this study. The effect of pumice amount (0.5-2.0 g), the effect of pH (3-8) and the effect of initial metal concentration (10-100 mg/L) were evaluated in the study. Taken samples were centrifuged for 5 min at 4000 rpm speeds before analysis.

2.3 Analysis

The prepared pumice composites were submitted to electron scanning microscopy (SEM)-energy dispersive X-ray analyzer (EDX) (FEI-QUANTA FEG 250) to obtained information about surface properties and chemical characterization of composites. SEM-EDX was operated at 2 kV accelerating at a constant magnification of 10000x. Merck test kits (Fe-114761 and Mn-114770) and UV–vis spectroscopy (Schimadzu UV-2401 PC) were used to analyze Fe and Mn at $\lambda=562$ nm and $\lambda=448$ nm wavelengths. The pH was monitored using a pH meter (WTW pH 315i).

3. Results and Discussion

3.1 Characterization of Pumice Composite

SEM analysis of pumice composite is demonstrated in Figure 1. Accordingly, pumice has porous and rough surface. According to EDX spectrums, pumice shows that oxygen and silicium are the major elements due to the origin of pumice characteristics that mainly contains 58.4% O, 29.5% Si, 6.7% Al, 1.4% K, 3.9% Na and 0.2% Fe.

Figure 1. SEM and EDX results of pumice
3.2 Effect of Activated Pumice Amounts

As shown in Figure 2, the removal of Fe was found to be approximately 100% at all amounts of P2 and P3 pumice composites whereas it was nearly observed at 100% using 1.5 g of P1 pumice composite in the single system. Nearly the same removal of Mn was observed using all pumice composites in the single Mn adsorption system. However, a rather lower removal efficiency was obtained using P1 pumice composite. In the case of binary adsorption systems, both Mn and Fe removals slightly decreased. Anyhow Mn and Fe removals increased with increasing the amount of pumice composites. The removal of both Fe and Mn was higher using P2 and P3 composites than P1 composite. Nevertheless, a gradually increasing removal trend of being 53.4%, 66.0 and 79.9% and 71.55%, 93.1% and 98.5% was observed for Fe and Mn respectively using 2 g P1, P2 and P3 composites correspondently. Fe removal increased from 23.8 to 39.5% by using acid activated kaolinite varying from 2 to 6 g/L (Bhattacharyya and Gupta, 2008).

![Figure 2. Effect of pumice amount using P1, P2 and P3 in the single and binary adsorption systems](image)

3.3 Effect of pH

As displayed in Figure 3, the pH is one of the most important factors influencing the process efficiency in the adsorption due to affecting both the surface charge of the adsorbent and the formation of metals. In this study, the influence of pH on Fe and Mn removals in the single and binary systems was investigated in the pH range of 3-11. Both Fe and Mn removals were found to be lower at acidic conditions than the alkaline conditions. Similar results were observed that higher Fe and Mn removal were observed at alkaline conditions by using untreated activated carbon and tannic acid modified activated carbon (Üçer at al., 2006). Removal of Fe and Mn
increased with increasing the solution pH up to 8. Fe removal using P2 and P3 pumice composites were observed to be nearly same but Fe removal using P1 was found to be lower than other composites used.

In the case of removal of Mn, maximum efficiency was obtained using P3 pumice composite (Fig.3). Accordingly, the performance order of composites used for Mn removal was to be P3>P2>P1. Although the same results were observed in the binary adsorption systems (Fig. 3), the adsorption capacity of Fe and Mn decreased compared to the single systems for all pumice composites. Mn and Fe adsorption capacities were calculated to be 1.62 and 9.00 mg/g for single adsorption and 1.03 and 7.23 mg/g for binary adsorption systems when P3 composite was used.

![Graphs showing Fe and Mn removal as a function of pH for single and binary systems.](image)

**Figure 3.** Effect pH using P1, P2 and P3 in the single and binary adsorption systems (Initial Fe or Mn concentration: 20 mg/L, pumice concentration: 2g; time: 24h)

### 3.4 Effect of Initial Fe and Mn Concentrations

Increasing initial metal concentration caused to decrease the removal of the metals due to the saturation of active sites on the pumice composites used (Fig. 4). Fe removal slightly decreased whereas the Mn removal was much affected by initial Mn concentration varying in the range of 10-100 mg/L. The removal efficiencies were observed at 96.8 and 84.8% for Fe 64.5 and 14.7 for Mn using P3 at 10 and 100 mg/L, respectively. Both Fe and Mn removals were found to be lower in the binary system than the single adsorption systems after a initial concentration of Fe and Mn concentration being 20 mg/L. Mn removal was affected higher than that of Fe removal comparing single and binary systems.
3.5 Langmuir Isotherm Evaluation

Fe or Mn adsorption fitted Langmuir isotherm at a high regression coefficient ($R^2 > 0.96$) as seen in Figure 5. Although Fe adsorption capacity was not significantly changed at different pumice composites, adsorption capacity of Mn was yielded 2.4 times higher using HCl activated pumice than $\text{H}_2\text{O}_2$ activated pumice composite use in the single adsorption system. Similar trends were observed in the binary adsorption system that is 2.2 times higher Mn adsorption capacity was observed using P3 compared to P1. These enhancing of adsorption removal were also shown in literature by using acid activated clays (Bhattacharyya and Gupta, 2008). Maximum adsorption capacities of Fe and Mn were observed using P3 in both adsorption systems. Fe and Mn adsorption capacities were found to be 9.00 and 1.62 mg/g in the single systems while they were calculated as 7.23 and 1.03 mg/g in the binary systems. These results indicated a higher capacity of pumice compoistes used than the results of zeolite and tannic acid immobilized activated carbon as reported by Motsi et al. (2009). They found out a 6.61 mg/g of Fe adsorption capacity while Mn adsorption capacity was reported to be 2.42 mg/g using natural zeolite. Furthermore, Üçer et al. (2006) reported that Fe and Mn adsorption capacities were 2.80 and 1.73 mg/g respectively using tannic acid immobilized activated carbon. Mn adsorption capacity was also obtained as 3.22 mg/g using montmorillonite, 4.22 mg/g mg/g using clinoptilolite and 2.54 mg/g using granular activated carbon (Abollino et al., 2003; Erdem et al., 2004; Jusoh et al., 2005). Although Mn adsorption capacity of activated pumice was found to be lower than all other adsorbents reported in the scientific literature, pumice could be evaluated to be more economical one (Cifci and Meric, 2016). If the adsorption capacity of Fe found in this study are compared with the literature, it is clearly seen that different values of 7.6 using clinoptilolite, 5.2 mg/g using chabazite, 4.1 mg/g using bentonite, 5.9 mg/g by kaolinite,
16.6 mg/g using montmorillonite were reported (Sheta et al., 2003; Bhattacharyya and Gupta, 2006). However, Fe adsorption capacity of pumice was found to be higher than the range given in the literature except the results of montmorillonite adsorbent.

![Figure 5. Langmiur Isotherm using P1, P2 and P3 f in the single and binary adsorption systems](image)

### 4. Conclusion

Removal of Fe and Mn increased with increasing pumice amounts and varying pH of the solutions. Fe and Mn removals were affected by activation acid type of pumice. HCl and HNO₃ acids were noted more effective ones than H₂O₂ in the single metal removal. In the case of binary system higher Fe and Mn removal were obtained using HCl activated pumice composite. Removal efficiencies of Fe and Mn were obtained in the order of HCl>HNO₃>H₂O₂. In conclusion, HCl acid activated pumice can be recommended to be more suitable and economic material for the removal Fe and Mn in both the single and binary adsorption systems.

### References


Investigation of Variation of the Recyclable Solid Waste Amounts in Küçükçekmece District of Istanbul

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Keywords: Küçükçekmece, recycle, reuse, solid waste management

Abstract

It is known that the amount of solid waste changes depending on the economical and cultural living conditions and also seasonal changes. In this study, the variation of recyclable solid waste amounts is investigated for the Istanbul Küçükçekmece district which has a high density of population and industrial activity. The recyclable solid wastes generated in study area are categorized as packaging wastes, waste batteries, waste vegetable oils and electronic waste and the variation of the amounts of these waste groups is investigated based on time between 2010-2015 years. When the amounts of recyclable and recycled packaging wastes are investigated, it is seen that show significant increases in years. While the amount of recycled packaging wastes was 3,876 tonnes for the year 2010, it reached to 77,601 tonnes in the year 2015 with a 20.02 fold increase. In the five-year period covering the period of the study, it is seen that packaging wastes form a large amount of the total wastes by analyzing the percent distribution of examined waste groups. The reason of that could be the simplicity of the recycling and reuse opportunities of packaging wastes. Recycling and reuse opportunities of the waste vegetable oils and e-wastes are new developing applications for this district. It is thought that the recycling ratio of this type of wastes will increase with the developments and improvements on waste management and collection systems.

1. Introduction

Recycling is the process of converting wastes to secondary raw materials following physical and chemical processes. It is also called as the conversion of the recyclable materials such as cardboard, plastic, paper, glass and metal to a raw material or product after passing through multiple processes. Prior to conversion process, the separation of wastes is needed according to their types (Ministry of Environment and Urban Planning, 2012). Energy production from recyclable wastes is significant in terms of economic benefits (Güler and Çobanoğlu, 1994).

Packaging is any material used to contain, protect, handle, transport and present raw materials or goods. Packaging waste includes all the materials including the wastes defined in Regulation on the Management of Packaging Waste and the other non-recyclable materials. Packaging waste includes boxes, pallets, crates, bags, sacks, tapes, disposable foodservice packagings and also items being used to handle or support the products being sold or to be sold (Regulation on the Management of Packaging Waste).

Waste battery is called as battery which has completed its useful lifetime or or unusable as a result of damage. Waste batteries should never be mixed with household waste. Therefore, waste batteries should not be disposed to the household trash. The outer cover of waste batteries
corrodes by time and the chemical materials and metals inside the battery spreads to soil and then into water. Heavy metals such as mercury and cadmium which is forming environmental pollution, damage living creatures consuming these contaminated foods. Different types of waste batteries should be separated according to their chemical structure. There are no waste battery recycling facility yet in use in Turkey. 'Regulation on the Management of Waste Batteries and Accumulators' was published by the Ministry of Environment and Forestry for the collection of waste batteries and accumulators on August 31, 2004. The responsibilities of battery manufacturers and importers and product distributors were defined by the Regulation (http://www.tap.org.tr, Access Date: 03.02.2016).

Vegetable oil wastes when they are discharged to sewage or water bodies, cover the water surface and damage the water system. It accelerates the oxygen depletion in water by blocking the oxygen transfer from air to water. It leads to cloggings in pipes and increase in operational costs in waste water treatment plants. Vegetable oil wastes is responsible from the 25% of total water pollution. The oil waste reaching to water bodies (sea, lake and river), harms fish, birds and the other creatures (http://cevreonline.com, Access date: 03.03.2016). The used oils must be collected separately from other wastes. It also should not be discharged to the receiving environment such as sewage, soil and sea.

Electronic waste (e-waste) is the type of waste generated from the completing of the life of electronic instruments and finishing the duration of use. E-wastes are commonly composed from computers, printers, phones, fax and photocopy machines, wires and medical equipments. The rapid development of technology today provides alternative materials and low cost recycling methods. The electronic instruments renewed by developing technology is defined as waste and they are used as secondary raw materials with the higher order compliance for recycling. Almost all of the E-wastes can be recovered with available recycling methods in order to prevent to cause major problems because of their toxic composition (Zhang and Xu, 2016).

2. Material and Method

Study area: Kucukcekmece district is located on the western side of Istanbul province. Kucukcekmece district having 37.75 km² area and 47.33 km perimeter, is located on major highways as Transit European Motorway (TEM-E80) and D100 (E5) that provide the Asia-Europe connection, as well as is located on the railway network which is centered in Sirkeci and extending to Europe. Istanbul Kucukcekmece district which has a high density of population and industrial activity. According to population data of 2015, 761,064 people live in the Kucukcekmece district (TUIK, 2015).

Collection of the data: The data of this study was formed by the arrangement of the data of domestic and industrial waste amounts reported regularly by the relevant units of the municipality on daily, weekly, monthly and yearly basis. In order to interpret the changes, the life styles of the population, the indoor and outdoor events held in the district, guest population of the district and the use of recreational areas are evaluated meticulously depending on the dates.
3. Results

The amount of packaging wastes collected by municipality shows large increases by the years in Küçükçekmece district boundaries (Figure 1). While the amount of recycled packaging waste amount is 3876 tonnes for the year of 2010, it is reached to 77601 tonnes with a 20 fold increase in the year 2015. In Figure 2, the composition of collected packaging wastes is displayed. It is composed from %12 plastics, %1 metals and %87 paper and cardboards.

Figure 1. Recycled packaging waste amounts

Figure 2. Material based distribution of collected packaging wastes
The amount of vegetable oil waste collected in Küçükçekmece district boundaries is showed fluctuations by the years (Figure 3). It has an increasing trend between the years 2010 and 2012, and it is reached to the highest value of the last six years in the 2012 year. There has been a decline in the years 2012-2014, then it is increased to 60980 tonnes value in 2015.

As seen from the Figure 4, the amount of waste batteries collected in the Kucukcekmece district boundary was followed by a scattered trend by the years. It has the lowest value in 2009 with 3660 kg and the highest in 2013 with 7635 kg.
Table 1. Percent distribution of collected recyclable waste groups between years 2010-2015

<table>
<thead>
<tr>
<th>Years</th>
<th>Packaging wastes</th>
<th>Waste batteries</th>
<th>Waste vegetable oils</th>
<th>Electronic waste</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>2010</td>
<td>43.97</td>
<td>55.51</td>
<td>0.52</td>
<td>0.00</td>
<td>100</td>
</tr>
<tr>
<td>2011</td>
<td>57.43</td>
<td>37.74</td>
<td>0.42</td>
<td>4.41</td>
<td>100</td>
</tr>
<tr>
<td>2012</td>
<td>79.79</td>
<td>16.30</td>
<td>0.30</td>
<td>3.62</td>
<td>100</td>
</tr>
<tr>
<td>2013</td>
<td>82.34</td>
<td>16.24</td>
<td>0.14</td>
<td>1.29</td>
<td>100</td>
</tr>
<tr>
<td>2014</td>
<td>90.11</td>
<td>7.10</td>
<td>0.07</td>
<td>2.72</td>
<td>100</td>
</tr>
<tr>
<td>2015</td>
<td>92.32</td>
<td>6.30</td>
<td>0.07</td>
<td>1.31</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 5. Amounts of recycled electronic wastes

In Figure 5, the amount of electronic waste collected in the Kucukcekmece district, has followed a trend of ups and downs by the years. While it has the lowest value as 600 tonnes in 2011, and it reached the highest value as 1838 tonnes in the year of 2014.

4. Conclusion

In the years that Küçükçekmece Municipality has organized training programs in order to raise public awareness, a significant increase is seen in the amount of recycled packaging waste, waste batteries, electronic waste and vegetable oil waste. It is thought that recycling awareness will be enhanced and lead to concrete results with periodical training programs in primary and secondary education institutions located in the district.

References

http://cevreonline.com, Access date: 03.03.2016


http://www.tap.org.tr, Access Date: 03.02.2016

Heterogenous Photocatalytic Treatment of Synthetic and Real Grey Water Samples for Reuse Evaluation

C. Kepoglu, C.B. Özkal, S. Meriç Pagano

Keywords: Greywater, Advanced oxidation processes, Photocatalysis, Reuse

Abstract

With respect to growing urban, agricultural and industrial water demand, reuse of wastewater (ww) has an utmost priority to overcome water shortage. Domestic wastewater is classified on the source basis and the literature is given insight with grey and black water definitions [1]. Reuse of GW for non-potable purpose such as irrigation, toilet flushing and groundwater recharge after proper treatment is widespread. Advanced treatment processes combined with biological treatment or an additional post treatment step is required. Also GW may contain recaltrant organic matter (anionic and cationic surfactants that are nonbiodegradable under anaerobic conditions) that may give rise to use of an Advanced oxidation process as a final treatment step [2,3].

The study is built on assessment of heterogenous photocatalysis efficiency on oxidative degradation of synthetic and real greywater samples. Efficiency of PC oxidation was examined based on DOC removal, UV254 ABS reduction levels namely the mineralization and degradation rates. Specific constituents of the synthetic greywater mixture was subjected to characterization studies, also taking into consideration the specific chemical composition of each individual. Increasing TiO$_2$ concentration from 0.1 to 1 g/L resulted with enhanced DOC removal rates. Reduction of GW suspended solid fraction by basic physical retention be it 24 hour of precipitation and 0.45 um pre-filtration, yielded enhanced photocatalytic DOC removal rates, where it is %27 for raw and %35 for filtered GW influent.

Introduction

Water pollution, water scarcity and in general the ongoing environmental deterioration has pushed research into eco-friendly and low energy cost efficient remediation. Conventional sewage treatment plants are projected and planned in a way to meet the required standards for removal of suspended solids, nutrients, organic matter and pathogens that are defined as conventional parameters.

A GW treatment system may necessitate different treatment steps that should be considered depending on the required quality of the effluent. For efficient, simple and economically affordable and sustainable treatment of greywater, generally a three step system consisting of an anaerobic-aerobic and disinfection step is recommended. Based on previous reports in the literature, treating GW BOD, COD load and pathogens only by filtering systems is not a feasible treatment application and not recommended. General water filtration technologies require a lot of energy to generate necessary driving forces to push water through membranes at high fluxes. In urban areas high water fluxes are necessary as the space for water treatment technology is limited and expensive in all Cities of the World. However the drawback of this approach is that high membrane fluxes need expensive pressure pumps, electronic process control, advanced
backwash and cleaning systems. At the same time high fluxes often cause rapid and serious colloidal and organic fouling in membrane systems [4]. Both factors make conventional filtration steps (often membrane based) costly for most water applications. Several emerging classes of micropollutants such as personal care products and drugs exist in wastewater and greywater matrices and conventional treatment systems are not sufficient in terms of total removal of these compounds (WHO 2006) [3,5]. Emerging pollutants, fate and transport of transformation products into aquatic environment, development and spread of antibiotic resistance in bacteria and ultimately the specification of the most effective technology that is capable of eliminating these kind of pollutants are the main focus points of recently ongoing international project partnership and scientific studies. Process efficiency should be handled by taking into account the eco-toxicity monitoring of the process effluent in virtue of which the process optimization would be more feasible [6–11]. Thus it is necessary to develop and implement new, simple and efficient technologies to generate high added-value tools offering sustainable processes and methodologies to meet water recovery requirements as well considering public health, occupational safety, environmental protection aspects. Hydroxyl radicals generated by AOP, follow unselective multi-step pathways which limit their efficiency in complex environmental matrices, with dissolved organic matter and carbonate/bicarbonate anions to be among the main hydroxyl radical scavengers in wastewater [12]. That would increase the scavenging rate of water together with the energy requirements for oxidation and disinfection. Photocatalysis (PC), that relies on the hydroxyl radical production with high reactivity, would tend to react micropollutants, re-calcitrants organics, most of organic-inorganic with high selectivity and rapidness that would end up with necessiated levels of total mineralization and conversion into less toxic products [13]. On the other hand, PC might not be considered an economically feasible alternative when the case is wastewater with DOM content. In such cases a pre-treatment step prior to oxidative treatment is necessiated and would enhance total efficiency of the system.

The aim of this study is to reveal potential treatment of real and synthetic (individual ingredients of real GW and two different synthetic mixtures with high and low COD values) greywater (GW) samples by photocatalytic oxidation with the intension of recycling and reuse possibility. The process efficiency was evaluated on the basis of DOC removal rates (mineralization), UV$_{254}$ absorbance removal (degradation).

**Materials and Methods**

**Samples and conservation**

Greywater samples (raw effluent, MBR effluent) and personal care and cleaning products were kindly provided from a 5 stars hotel located in Antalya city, Turkey. Samples were transferred to the respected Laboratory and kept cooled at +4°C during experiments without adding any conservative chemical.

**Photocatalytic experiments**

**In order** to find out if photocatalysis is an alternative to conventional step procedure of water purification systems and filtration systems or it is a better choice when adapted with a well optimized integration into existing treatment options, studies should be intensified not only on raw grey water samples but also on effluents of existing GW treatment options. With this purpose studies intensified on assessment of exact place of the proposed process within the existing process flow. This would be a pioneering approach and necessitate appropriate survey and experimentation. In this manner MBR treated effluents of GW samples were subjected to PC treatment, prior to 24 h sedimentation and 0.45 um filtering steps. Since the efficiency of
heterogenous photodegradation depends on the contact between the surface of the catalyst and target compounds, we set the focus on homogenous photocatalysis process at neutral pH such as, TiO2 photocatalysis (PC). Photocatalysis is applied in a multilamp photoreactor with the use of Degussa T25 TiO2 as the photocatalyst with dosages of 0.1 to 1 g/L. Level of UV energy applied was kept in comparable interval with the literature findings that are mainly based on PC degradation of varying micropollutants (4.94 mw/cm²²) [13,14]. UV absorbance measurements at 254 nm wavelength were taken as indicators of degradation of organics while DOC as representative of total rate of mineralization.

**Analysis**
The incident of photon flux was measured by Universal Photometer. Photocatalytic oxidation and degradation of greywater also with the formation of oxidation by-products were monitored by UV absorbance (Schimadzu, UV-1800). Mineralization was determined by TOC measurement (Schimadzu, 6KVA model). pH was also monitored (Hach Lange multi parameter) to better evaluate mechanism and efficiency of the photocatalytic oxidation [15].

**Results and Discussion**

**Characterization of the samples and the synthetic solutions**
The characteristics of the samples are presented in Table 1. Table 2 provides insight into individual ingredients and their composite mixture (CM).

**Table 1. Characteristics of the greywater samples used in the study**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>MBR influent</th>
<th>MBR effluent</th>
<th>Chlorination Effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity</td>
<td>(mS)</td>
<td>499</td>
<td>511</td>
<td>435</td>
</tr>
<tr>
<td>TDS</td>
<td>(ppm)</td>
<td>250</td>
<td>256</td>
<td>218</td>
</tr>
<tr>
<td>Salinity</td>
<td>(ppt)</td>
<td>0.23</td>
<td>0.24</td>
<td>0.20</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>7.03</td>
<td>7.1</td>
<td>7.02</td>
</tr>
<tr>
<td>Suspended Solids</td>
<td>(mg/L)</td>
<td>19.6</td>
<td>5.1</td>
<td>3</td>
</tr>
<tr>
<td>COD</td>
<td>(mg/L)</td>
<td>135</td>
<td>&lt; 30</td>
<td>&lt; 30</td>
</tr>
<tr>
<td>Soluble COD (0,45 u)</td>
<td>(mg/L)</td>
<td>105</td>
<td>&lt; 30</td>
<td>&lt;30</td>
</tr>
<tr>
<td>NH3-N</td>
<td>(mg/L)</td>
<td>0.896</td>
<td>0.056</td>
<td>0.056</td>
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</table>
Table 2. Characterization of mixture and individual constituents of synthetic greywater sample.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
<th>S5</th>
<th>S6</th>
<th>CM</th>
<th>CM*</th>
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</thead>
<tbody>
<tr>
<td>Conductivity</td>
<td>(mS)</td>
<td>25.4</td>
<td>24.8</td>
<td>98.8</td>
<td>18.73</td>
<td>4</td>
<td>35.1</td>
<td>594</td>
<td>451</td>
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<tr>
<td>TDS</td>
<td>(ppt)</td>
<td>12.8</td>
<td>11.8</td>
<td>49.5</td>
<td>9.37</td>
<td>2.0</td>
<td>17.6</td>
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<td>245</td>
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<td>Salinity</td>
<td>(ppt)</td>
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<td>10.36</td>
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<td>0.19</td>
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<tr>
<td>pH</td>
<td>--</td>
<td>6.45</td>
<td>6.36</td>
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<td>11.8</td>
<td>5.75</td>
<td>8.45</td>
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<tr>
<td>TOC</td>
<td>(mg/L)</td>
<td>109.8</td>
<td>55.8</td>
<td>39.5</td>
<td>13</td>
<td>18.75</td>
<td>47.5</td>
<td>280.3</td>
<td>76.28</td>
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<td>NH3-N</td>
<td>(mg/L)</td>
<td>560</td>
<td>5</td>
<td>3.5</td>
<td>42</td>
<td>28</td>
<td>456.4</td>
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<tr>
<td>Xenobiotic</td>
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<td>pentylene</td>
<td>poliphos</td>
<td>n.a</td>
<td>n.a</td>
<td>sodium</td>
<td>[16,17]</td>
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<td>benzyl salicylate</td>
<td></td>
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</tbody>
</table>

(S1: Shampoo and shower gel, S2: Liquid soap, S3: Chloric cleaning product, S4: Acidic cleaning product, S5: Alkali saniter ground cleaner, S6: Shower gel, CM: contains 1 mL of each individual products in 1 L distilled water, CM*: Diluted CM at 1/3 (v/v) in distilled water), Reported chemical components of individual constituents for the synthetic GW sample were provided with the known effect on PC mechanism, Chemical components known to cause inhibitive effects are given as bold text, while the ones with standard text are reported to enhance PC activity. [16,17]

Photocatalytic treatment

Increasing TiO$_2$ dose resulted in enhanced mineralization rates (DOC removal %) for the real GW sample that was collected by separated system. Using 0.1 to 1 g/L of initial TiO$_2$ resulted in %10 to %28 DOC removal) as can be seen in Figure 1, similar enhancement in organics removal as a response to increasing photocatalyst dose were reported elsewhere [18,11]. While at 0.5 g/L TiO$_2$ initial conditions, the highest PC removal efficiencies were achieved (%30) on the precipitated GW samples that are theoretically free of suspended solids, namely in the conditions where colloid based competition for the active surface sites are negligible, where it was the case reported in literature when wastewater samples with relatively high initial organic load was subjected to heterogenous TiO$_2$ PC oxidation [11].

A physical retention step before the PC treatment has been experimentally studied on real GW samples. The efficiency of DOC removal increased by %27 %28, %35 in the PC treated sample applied to raw, precipitated (24 h) and filtered (0.45 um) GW samples respectively at 120 min of PC oxidation applied using 0.5 g/L TiO$_2$. The xenobiotic componentes of GW be it sodium laureth sulphate, benzophenone-4, benzyl salicylate, citronellol, polyphosphates etc. mostly known to be causing inhibitive effects on photocatalysis mechanism, on the other hand Polyethylene glycol and derivatives reported to be enhancing PC photodegradation, characterization findings of which is presented in Table 2. These components have been theoretically retained in the 0.45 um cellulose acetate filters and resulted with an overall enhancement of PC activity, resulted with %35 of DOC removal efficiency [16,17]. These findings clearly indicate that even small components at typical concentration found in GW household effluents have potential to cause inhibitive/ enhancing effect on PC activity. Photocatalytic efficiency was compared at two different sources of GW be it synthetic CM, and real GW at their natural pH and 0.5 g/L TiO$_2$ conditions. Regarding DOC removal rates at 30-
120 min, both sources of GW seem to play an analogous role on photocatalytic mechanism. As is seen in Fig. 2 by comparable efficiencies obtained; %39-48 for CM, CM* at 30 min. And %56-74 and 27 for CM, CM* and real GW after 120 min. Concerning its more complex nature, real GW provided a more inhibitive effect on the photocatalytic mechanism [16,19]. Generally the observed PC performance findings are in the comparable range with the efficiencies obtained by existing treatment technology MBR+chlorination of matter (%70-75 COD Removal) Sanchez et. Al and Zhu et. al have successfully applied and achieved over %60 DOC removal rates with surface immobilized and heterogenous TiO2 Photocatalysis on real and synthetic GW samples respectively[20,21].

**Fig. 1** Effect of catalyst concentration on photocatalytic degradation and mineralization in real greywater samples exposed to 4.94 mw/cm² UV-A energy at pH: 7.03.

**Fig. 2** Effect of different pre-treatment alternatives and GW source on photocatalytic UV254 and DOC removal rates. 4.94 mw/cm² UV-A energy. Given the abbreviations GW: Greywater sample, CM : Composite mixture, CM* : 1/3 Diluted Composite mixture, Precpt: GW sample subjected to precipitation, Filt: GW sample subjected to 0.45 micron filtration.

**Conclusion**

Emphasizing that removal of certain hazardous pollutants (be it micropollutants-xenobiotics etc.) by filtration and or biological treatment options would be very costly and unfeasible and in order to overcome filter type and structure based limitations, combination of photocatalytic degradation with proper pre-treatment methodology is a promising approach. As it is seen by the obtained DOC removal rates for real, synthetic and diluted synthetic grey water samples, it
can be noted that organic load and photocatalyst dose are determining factors on PC mineralization rates, while specific individuals of grey water may play a significant role on oxidative process mechanism and should be monitored and managed accordingly.

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References


Assessment of thin-film photocatalysis inactivation of different bacteria strains and variation in antibiotic resistance behaviour

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Keywords: Thin-Film, Photocatalysis, Parallel Plate Reactor, Antibiotic resistance, MIC, Inactivation

Abstract

Presence of pathogens in water bodies endangers access to freshwater sources and necessitates the proper inactivation of target organism with a proper disinfection technology. Advanced oxidation processes (AOPs) have become emerging treatment options to remove both different kind of target pollutants and pathogens in parallel effectively. Among AOPs, both suspended and immobilized photocatalysis systems are still in question about being under control of different interactions between the photocatalyst and the target pollutant(s). The present study is to assess of TiO2 based thin film photocatalytic inactivation and consequence in the variation of antibiotic resistance. Effect of varying process parameters on bacteria inactivation was tested in a flat plate photoreactor taking into account the type and origin of bacteria strains and the initial bacteria concentration. A stationary phase of bacteria inactivation proceeded with a rapid and efficient one for the case of E. faecalis ATCC-14506, while the trend is more like extended over process period (time) for the scenario with Escherichia coli reference strain DSM-498 [3,4]. Among the tested antibiotics considerable changes in MIC values were recorded for beta-lactam (Ampicillin and Cefaclor) and macrolide (Clarithromycin and Erythromycin) group antibiotics.

Introduction

Photocatalysis is a promising sustainable green photochemical process which is also able to provide acceptable levels of bacteria inactivation [5–7]. Based on cost, chemical and photochemical stability, availability, and reduced toxicity considerations TiO2 is reported to be the most suitable photocatalyst to date for disinfection of water [3]. However, both suspended and immobilized photocatalysis systems are still in question about being under control of different interactions between the photocatalyst and the target pollutant(s) [8,9]. Within this scope, proper design of a reactor/system is critical issue since the interaction between the catalyst, target pollutant and light will be directly influenced by flow regime and operation conditions of the reactor. Longevity findings reported so far and non-requirement of separation from the system make immobilized systems superior compared to suspended system photocatalysis applications [10]. To ensure that larger scale photocatalytic (PC) disinfection applications/reactors become widespread, assessment of process parameters affecting photocatalytic activity, stability and replicability of the photocatalytic performance under controlled conditions, development of proper reactor configuration are some fields that still require intense research [10,11]. By this means range of process applicability should be tested taking into account different type and source of bacteria. The recycling batch mode of operation for bacteria inactivation with immobilized photocatalyst system (with the vertical formation at cross section; PC surface, solvent matrix containing bacteria cells, >%90 transparent pyrex glass and UV irradiation from bottom to top by order) is a pioneering approach which was previously reported with replicable experimental conditions on degradation of micropollutants in the same mode of operation [37]. This study aimed to test a thin film based flat type
photocatalytic reactor for inactivation of environmental isolates of (Gram(+)) and (Gram(-)), bacteria that initial bacteria concentration were selected as the parameter of concern. Besides the estimation of level and type of different parameters, antibiotic resistance profiles of non-treated and intact cells (exposed to PC treatment) have been determined based on observed variations in minimum inhibitory concentration (MIC) values for selected group of antibiotics of Ampicillin and Cefaclor, Clarithromycin and Erythromycin.

2. Materials and Methods

2.1. Thin film

Polyethylene glycol enriched Titanium tetraisopropoxide based TFs were fabricated and used in PC experiments [12]. The TiO$_2$ loading density was kept between 0.064-0.096 mg/cm$^2$ based on gravimetric analysis [13,14].

2.2. Photocatalytic reactor

The reactor was designed and produced with the intent of providing fully plug-flow conditions that has no recirculation or dead-zones along the reactor. The reactor consists of two plates at the top and at the bottom. As indicated in the literature the PPL model is one of the most efficient configuration and it was possible to actualise a differential reactor model with the proposed reactor configuration [15–18].

2.3. Bacteria isolates

The bacterial strains of *E. coli* DSM-498 and *E. faecalis* ATCC-14506 were tested to inactivate. In parallel, environmental isolates of *E. coli* and *Enterococcus sp.* were also tested. Those strains were isolated from seawater samples, taken in Chania, Greece through the filtration methodology decribed elsewhere [38].

2.4. Photocatalytic inactivation

The procedure described within the serial dilution standard methodology indicate the necessity of using %0.08 NaCl (w/w basis) solution for dilution of the bacterial solutions prior to their cultivation into agar plate, in order to minimize the physical stress conditions (be it osmotic pressure) that the bacteria cells may be exposed. The effect of solvent matrix was examined at varying initial NaCl concentration levels [22–24]. Inactivation rate of *E. coli* and *Enterococcus faecalis* at an initial concentration of $10^5$ CFU/mL was detected and enumerated by the serial dilution streak plate procedure [39]. Preliminary photolytic experiments were performed by applying UV-A exposure to bare (uncoated) glass that have been replaced with TF coated glass substrate. Flow rate is a determining factor for the contact time between the PC surface and bacteria cells, and also for total time of irradiation per single pass effective on unit volume of solution, thus it has to be optimized. Subsequent to setting proper intervals to operate immobilized flat plate reactor, replicability of the TF PC performance was adressed based on the determined rate of bacteria inactivation in consecutive runs [12,37].

2.4. Antibiotic resistance

Antibiotic resistance profile of the reference and PC treated bacteria was examined applying the broth microdilution method and estimating the Minimum Inhibitory Concentration (MIC) of selected antibiotics namely Levofloxacin, Erythromycin, Clarithromycin, Cefaclor, Amikacin, Sulfamethoxazole and Ampicillin [19–21]. Before beginning with effect assessment of selected factors on obtained bacteria inactivation efficiencies, a pre-liminary experimentation has been carried out in order to optimize basic parameters of the process be it flow rate, Uv energy level, initial anion concentration.
3. Results and Discussion

3.1. Preliminary Experimentation

UV-A energy of 0.94 mw/cm$^2$ was found to be the optimum value for the elimination of the tested bacterial strains beyond the process of photolysis as can be seen in Figure 1. The ion concentration value of 8 g/L is well above the minimum value that is reported to be giving rise to inhibited PC activity [22–24]. Since the survival rate observed after 4 hours of photolysis is more or less the same, the physical stress conditions did not act as a predominate factor (Fig. 1) Experiments under varying UV energy levels were carried out with *E. coli* DSM-498 strain that showed a 0.90 mw/cm$^2$ should be set as the limit value (Fig. 1-b).

![Figure 1](image_url)

**Figure 1.** Photocatalytic Bacteria inactivation rates for a) varying initial NaCl concentration at UV-A energy: 0.90 mw/cm$^2$, b) for varying UV-A irradiation levels: [C]$_{NaCl}$ : 0.008% w/w. Initial conditions for both: Initial *E.coli* DSM-498 bacteria concentration; 105 CFU/mL, Flow rate: 90 mL/min, regeneration procedure with distilled water+H2O2 %0.1 v/v + UV-A.

Flow rate was optimized considering references run at the same reactor configuration for the case of micropollutants degradation [12,37]. Increased flow rate ended with decreased PC bacteria inactivation rates (Fig. 2). The interaction between bacteria cells and photocatalyst surface has the utmost importance since the dominant mechanism responsible for PC bacteria inactivation is the interaction between surface adsorbed bacteria cell and reactive oxygen species (ROS), mainly OH radicals (OH) as it is most frequently reported in literature [26–28]. Stability of TF photocatalytic activity was slightly observed between different cycles with the same TFs. TF coated surfaces may contain some impurities following the fabrication procedure and they were subjected to an initial cleaning procedure [12,37] Efficiency of regeneration procedure has been well demonstrated as seen in Fig. 2-b. The inactivation rate decreased during 4 th cycle of PC run [29].
3.2. Effect of Different Type & Source of Bacteria on PC Bacteria Inactivation

Cell structure is reported to be more complex for gram(-) bacteria but inactivated less efficiently compared to gram(+) indicating cell wall destruction may not be necessary for inactivation [14]. Amrita et al. (?) performed bacteria inactivation experiments in a configuration with immobilized TiO$_2$ on membrane structure, and at 234 mg/m$^2$ TiO$_2$ and 0.013 mw/cm$^2$ UV-A irradiation conditions, $>%90$ inactivation of $E$.coli K12 bacteria was observed at the end of 30 min when photocatalytic inactivation rate of Gram(-) bacteria ($E$.coli) was higher than Gram(+) bacteria. The findings were comparable with the study of Pal et al. who achieved $>%90$ inactivation of $E$.coli under 0.8 mw/cm$^2$ UV-A irradiation after 20 min in the presence of TiO$_2$ [14]. On the contrary, there are such literature findings claiming that inactivation of Gram(+) bacteria is more efficient compared to Gram(-) bacteria, that is in accordance with our experimental results (Fig. 3) [4,10,14]. Besides, PC activity was reported to be higher for the most hydrophobic bacteria when immobilized catalyst was used. Due to high hydrophilicity of $E$.coli, other Gram (-) bacteria, more hydrophobic than $E$.coli or Gram (+) bacteria itself were reported to show more adherence and interaction with the immobilized catalyst [4,30]. These literature findings are also in accordance with the $E$. faecalis inactivation results (Fig. 3). For the case of observed differences between photocatalytic inactivation of laboratory and environmentally isolated strains, one should note that diversity of protein structures and their exact positions arising from level, type and duration of exposure to environmental stress in their background may play a major role in their inactivation mechanism. (Fig. 3-b) [25,31]. Same instructions are assumed to be valid and significant in the case of different antibiotic resistance profiles exhibited by intact cells and cells belong to post treatment [32].
3.3. Effect of Initial Bacteria Concentration

For the case of Photocatalytic inactivation of E.coli DSM-498 bacteria, a general trend of increasing bacteria inactivation rates and % bacteria inactivation (%90-98->99 respectively) were obtained for higher initial bacteria concentration (10^3 to 10^7 CFU/mL). As shown in Fig. 4 inactivation followed a pseudo zero order (PZO) reaction [33,34].

3.4. Effect of Photocatalytic Treatment on Antibiotic Resistance Profile of Bacterial Strains

Antibiotic resistance profile was affected to a certain extent, depending mainly on the antibiotic and the strains tested as seen in Fig. 5 [19,20,25]. The alteration of MIC values after treatment may raise concerns regarding public health, especially if the resistance of the bacterium becomes higher. Underlying the non-selective mechanism of photocatalytic oxidation, ROS that is present both in the solvent matrix and on the surface of photocatalyst, would oxidize porin and protein structure of target bacteria cells in a random manner (initial effect). In the case of H_2O_2 and OH radical formation, both base and ribose moieties of the DNA get oxidized (cell membrane effect) and the cell repairment mechanism get almost inactivated [32].
Fig. 5. Antibiotics on the growth inhibition of the residual cells of the tested bacterial strains post treatment.

Conclusion
Wide range applicability of thin-film photocatalysis on bacteria inactivation have been examined taking into account the different type and sources of bacteria strains. Environmental isolates of E.coli displayed more resistance to oxidative conditions compared to standart laboratory strains. Initial concentration is found to be a determining but not a limiting factor on PC disinfection mainly for the case of Gram(-) bacteria. Antibiotic resistance profile of intact and post-treatment bacteria cells are indicating that PC oxidation mechanism is also effective on the resistance behaviour of target bacteria. While environmental isolates of E.coli is less sensitive to changes in antibiotic resistance behaviour that is in compliance with the main findings regarding total PC inactivation rates of laboratory standart and environmental isolates of E.coli.

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References


Wastewater Reuse Potential of Paint Operations in an Oven Manufacturing Plant

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Keywords: Reuse; wastewater; paint; oven manufacturing.

Abstract

The objective of this study is to assess the wastewater reuse potential of paint operations in an oven manufacturing plant. A detailed quantitative and qualitative characterization related to the water input and wastewater output is performed to reach the goal of the study. The results obtained indicates a reusable wastewater generation potential of 126 m$^3$/day. This amount corresponds to 57% of the total wastewaters generated from the paint operations.

1. Introduction

Annual industrial water consumption accounts for 11% of the total water consumption of the Turkey (MoEF, 2010). In other words, annually 5 billion m$^3$ of water is used by Turkish industry (MoEF, 2010). This amount is expected to increase drastically and reach 22 billion m$^3$ in the next 15 years. Such an elevation in industrial water demand necessitates proactive precautions. Especially sectors with high water consumption levels must tackle their own water scarcity pitfalls. Besides, actions covering the wastewater reuse may yield both economic and environmental benefits for industrial sectors that consume high amounts of water. Metal coating industry is among sectors that require high amounts of water input.

In this context the objective of this study is to evaluate the wastewater reuse potential of paint operations in an oven manufacturing facility. For this purpose, process profiles together with pollution profiles are investigated by performing a detailed quantitative and qualitative characterization of the inputs and outputs.

2. Materials and Methods

All the segregated wastewater samples are obtained from an oven manufacturing facility that conducts paint operations. The conventional wastewater characterization is performed on the segregated effluent streams of three different painting processes (Silver, white-black and anti-finger). In the characterization study, conductivity, pH, total organic carbon (TOC), Fe, oil and grease, calcium, magnesium, hardness, silicon, chloride, nitrite and nitrate measurements are performed out on grab wastewater samples collected from segregated effluents. The chemical oxygen demand (COD) measurements are conducted according to ISO 6060 method (ISO, 1986). The Standard Methods are applied for the analysis of all the other parameters (APHA, 2005).

244
3. Results and Discussion

The paint process is chosen as the target of this study as it has the highest water consumption among others.

In the painting operations, parts of oven that are previously exposed to 200°C temperatures are painted. Silver, white-black and anti-finger processes are the specific painting processes that are classified under the paint operations. Silver and white-black processes are named according to the color of the applied paint. On the other hand, anti-finger process is related to operations that give the products a stain proof characteristics of fingerprints. In the facility, there also exists a powder painting line where automatic paint guns are used. As powder painting is a dry process that is not generating any effluent, it is beyond the scope of this study. The process flow chart of white-black, silver and anti-finger lines are given in Figure 1, 2 and 3, respectively. Segregated wastewater characterization of these three lines are tabulated in Tables 1-3.

Figure 1. Process flowchart of white-black line
The water requirements of all the paint operations are 83,744 m$^3$/year. The wastewater characteristics are evaluated by considering the flowrates and quality requirements of process waters namely softened and distilled (DI) water. The water is supplied from a well. From paint operations 80,124 m$^3$/year of wastewater is generated. As given in figures, in all paint processes there are continuous water requirements together with intermittent ones that are mainly applied for cleaning purposes, resulting in continuous and intermittent wastewater generations.

According to the detailed segregated wastewater characterization, the reusable wastewater generation potential of paint process is evaluated to be 126 m$^3$/day. This amount accounts for 57% of the total wastewaters generated from the paint operations. It is recommended to perform treatability studies on this reusable wastewater fraction.
Table 1. Segregated wastewater characterization of white-black line

<table>
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<th>I1</th>
<th>I2</th>
<th>I3</th>
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<th>I4</th>
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<th>I6</th>
<th>I7</th>
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<th>C4</th>
<th>I10</th>
<th>I11</th>
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<th>C3</th>
<th>C13</th>
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247
Table 2. Segregated wastewater characterization of silver line

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<td>785</td>
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<td>110</td>
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<td>561</td>
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<td>152</td>
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<td>&lt;10</td>
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<td>Fe (mg/L)</td>
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<td>30</td>
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<td>286</td>
<td>746</td>
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<td>77</td>
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Table 3. Segregated wastewater characterization of anti-finger line

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<td>240</td>
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Table 4. Required process water quality

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<td>Nitrite</td>
<td>mg NO₂/L</td>
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<tr>
<td>Phosphate</td>
<td>mg PO₄/L</td>
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Acknowledgements

This research was supported by The Scientific and Technological Research Council of Turkey (TUBITAK) Research Project (No: 5130059).

References


Single and Binary Adsorption of Copper and Nickel Metal Ions on Nano Zero Valent Iron (nZVI)

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\textsuperscript{a} Yildiz Technical University, Environmental Engineering Department, Istanbul, Turkey

Keywords Adsorption, Nano-Zero Valent Iron (nZVI), Nickel Removal, Copper Removal

Abstract

Copper and Nickel have been concerned intensively due to their persistent, non-biodegradable and toxic characteristics. This present study concerns adsorption of copper (Cu(II)) and nickel (Ni(II)) ions onto nano zero valent iron (nZVI) from single and binary systems. Except from low efficient conventional adsorbents, nanoparticles such as nZVI, carbon nanotubes are promising adsorbents by having higher adsorbent surface area and nano sized pores. Removal efficiencies are investigated for single and binary adsorption by considering initial concentration of copper and nickel. While the removal of copper was high as 92% with the absence of nickel ion in aqueous solution, it was decreased to 61% with 50 mg/L nickel ion concentration. In a similar manner, 88% removal rate of nickel ion with absence of copper was decreased to 70% with 50 mg/L copper ion concentration. Higher metal ion concentrations effected even worse by having 26% of removal efficiencies or less. It is also observed that adsorption capacity of copper ion is higher than nickel ions in binary system. For highest total metal ion concentrations (300 mg/L) adsorption capacities are obtained as 1060 mg/g and 1010 mg/g for nickel and copper adsorption in binary system, respectively.

1. Introduction

Nickel and copper are materials used especially in electronic industries and they attempt to ecological system and bioaccumulate. Nickel is mostly known as causing lung and nasal cancer. Because of having persistent characteristic, it is difficult to treat heavy metals by biological or chemical degradation.

In the literature, several methods such as adsorption [1-4], membrane filtration [6-7] and electroflocculation [8] have been applied for nickel and copper ions. Although many studies are performed for heavy metal treatment by activated carbon, removal in lower concentrations is considerably low [9-10]. Except from these low efficient conventional adsorbents, nanoparticles such as nano zero valent iron (nZVI) and carbon nanotubes [11-14] are promising adsorbents by having higher adsorbent surface area and nano sized pores.

Nanotechnology has attracted considerable attention in environmental engineering practices due to their properties such as high adsorption capacity and rapid responses. While the most applied application of nanotechnology in this field is soil remediation, water and wastewater treatment facilities became popular. On heavy metal removal, studies show that nZVI is effectively used on heavy metal adsorption [12-13].

While adsorption of heavy metal by nanoparticle are widely studied in single systems, this present study concerns adsorption of copper (Cu(II)) and nickel (Ni(II)) ions onto nano zero
valent iron (nZVI) from single and binary systems. In single adsorption system, pH effect was investigated for both nickel and copper ions. Further studies were conducted by determined optimum pH. While the effect of adsorbent concentration was investigated in single adsorption system, effect of initial metal ion concentration was investigated in binary system. For binary system, in order to observe interactions between copper and nickel ion, it is studied with 5 different concentrations of both metals.

2. Materials and Methods

2.1 Nanoparticle Synthesis

In this study nZVI was synthesized using borohydride method, in which the borohydride method is the most common method [15] as performed in the reaction given below.

$$\text{Fe}^{2+} + 2\text{BH}_4^- + 6\text{H}_2\text{O} \rightarrow 2\text{Fe}^{0} + 2\text{B(OH)}_3 + 7\text{H}_2\uparrow$$

FeSO$_4$.7H$_2$O solution was dissolved in water:ethanol (30:70, v:v) mixture. In order to prevent aggregation, the method was enhanced by adding PEG. Borohydride solution was added dropwise with rate of 30 mL/min to iron sulfate solution. After obtaining nanoparticle, mixture was wash with ethanol and pure water in order to inhibit negative effects of SO$_4^{2-}$ and Br$^-$ ions. Particle size of nZVI was measured as 68.7nm by zeta sizer. TEM images of the produced nZVI also showed that nZVI has a spherical and chain structure.

![Figure 1. TEM image of nZVI](image)

2.2 Experimental Studies

All experiments were studied with synthetic samples prepared by CuSO$_4$ and NiCl$_2$.6H$_2$O (MERCK). In single adsorption system, the experiment sets were conducted in 100 mL total sample volume with different concentrations of nZVI concentration. In binary system, experimental sets were contained in optimum pH and concentration of nZVI and shake at 150 rpm and 20 °C constant temperatures for 30 minutes. Resulted samples were centrifuged at 6000 rpm for 5 minutes for separation of nanoparticles. The initial and effluent copper and nickel analysis were applied in Perkin Elmer Atomic Adsorption Spectrometer C-400.
3. Results and Discussion

3.1 Single Adsorption of Nickel and Copper

3.1.1 Effect of Initial pH

Experimental setup was conducted to state pH effect on removal of copper and nickel in single adsorption, in which pH was adjusted pH 2 to 12. Concentration of synthetic samples was 100 mg/L and applied adsorbent concentration was 100 mg/L for 30 min of reaction time.

As seen in Figure 2.a, the removal rates for nickel in pH 6 and 7 was 63% and 68%, respectively. There was any significant changes in removal rates with higher pH than pH 7. Similarly, it can also be seen in Figure 2.a that the removal rates was considerably low with the pH adjusted lower than pH 6. However in copper removal, removal rates were obtained as 80%, 80% and 99% for pH 6, 7 and 8, respectively. In the experiments with higher pH than pH 8, removal rate was almost 100 %. This can be explained by hydroxyl reaction and hydroxyl settlement with copper in high pH. With the light of obtained data, the further study was established with pH 6, 7.5 and pH 6, 9 for nickel and copper samples which are the original pH of each samples.

Effluent pH and difference between initial and effluent pH was also observed as given in Figure 2.b. While there was not considerable changes in effluent pH with the studies applied in pH 6 and pH 7, the studies with lower and higher pH values than pH 6 and 7 there were substantial changes especially by increasing to pH 7 for lower initial pH and vice versa. In higher initial pH concentration than pH 7, the decreasing in effluent pH can be caused by the rapid reaction of metal ions with hydroxide via formation of metal hydroxides [16]. Correspondingly, the high concentration of H⁺ in lower initial pH can caused to corrosion of nZVI by consuming water to generate OH⁻, therefore the effluent pH in low initial pH is increased.

3.1.2 Effect of Adsorbent Concentration

By arranging initial concentration of Ni and Cu in 100 mg/L for each sample, the effect of adsorbent concentration was investigated. Experiments were conducted in 100 mL of sample volume in 150 rpm for 30 minutes. Selected concentrations for nZVI were 50, 100, 200 and 400 mg/L. The obtained removal rates and calculated adsorption capacities can be seen in Figure 3.
It can be gathered from Figure 3 that, removal rates for each samples were increased with adsorbent concentration as expected. A slight increase was obtained between 200 and 400 mg/L adsorbent concentration for copper samples. This gives the information about optimum adsorbent concentration for copper removal.

While it is observed a linear increase in a slight rate with increased adsorbent concentration for nickel removal, 200 mg/L nZVI concentration was selected for both nickel and copper removal for the comparison with the data in binary adsorption experiments.

Adsorption capacities can also be seen in Figure 3. Both ions give similar responses with nZVI. Highest adsorption capacities were 704 and 720 mg/g for 100 mg/L concentration of nickel and copper, respectively.

![Figure 3](image)

**Figure 3.** Removal rates and adsorption capacities of Cu(II) and Ni(II) in nZVI concentration variations

### 3.2 Binary Adsorption of Nickel and Copper

With the light of the data obtained in single adsorption system, the binary system was accompanied with different copper and nickel concentrations and their effect to each other. Matrix was prepared with 10, 25, 50, 100 and 150 mg/L concentrations of copper and nickel ions to detect the effect of copper ion concentration on nickel ion removal, and vice versa. Single metal adsorption is also studied for both metal ions in order to compare data in binary system.

In Figure 4, effect of copper concentration on nickel removal can be seen. High decrease in removal rate is observed in binary system (removal of copper and nickel ion in same sample) than single metal adsorption system. In the studies with 10, 25 and 50 mg/L nickel concentration without copper ion the removal rates was 88, 85 and 81%, respectively; while the lowest studied concentration of copper concentration (approximately 10 mg/L) is applied, removal rates was decreased to 81, 78 and 70% for 10, 25 and 50 mg/L initial copper concentration, respectively. In the studies with higher initial concentration of copper than 25 mg/L, high decreased in nickel removal was observed. The lowest removal rate of nickel was obtained with the sample containing 150 mg/L copper and 150 mg/L nickel ions and it was 20%. In addition, it is also be noted that, higher than 70% removal rate is observed for 150 mg/L copper concentration in single adsorption. Comparably to nickel removal, effect of nickel concentration in copper removal is given in Figure 5. The removal rates of copper with
10, 25 and 50 mg/L in single adsorption system was approximately 92%. With the addition of nickel ion in concentration of 10 mg/L, removal rates was decreased to 86, 76 and 61%, respectively. Decrease in nickel removal was lower than copper removal. With higher initial nickel concentration than 25 mg/L for all copper concentrations, the decrease in removal was considerably low when it is compared to nickel removal. The removal rate of copper was lowest as 26% with 150 mg/L initial concentration of both nickel and copper. Moreover, it should be remarked that, for single nickel adsorption, removal rate was higher than 70% with initial nickel concentration of 150 mg/L.
Adsorption capacities were calculated by considering adsorbed metal ion in total metal ion concentration. Figure 6 is presenting nickel and copper ion adsorption capacities. Adsorption capacities were increased with the increase in total metal ion concentration, as expected. For the highest total metal concentration of 300 mg/L (150 mg/L nickel and 150 mg/L copper ion concentration) adsorption capacities were 1060 and 1010 mg/g for nickel and copper, respectively. For all experiments adsorption capacities for both metal were almost similar.

Conclusion

For single adsorption system, adsorbent concentration of 100 mg/L nZVI is sufficient for 100 mg/L metal ion concentration, and also with higher adsorption capacity (approximately 500 mg/g) than conventional adsorbents such as activated carbon. Synthesized nZVI is a promising adsorbent even in high concentration of nickel and copper metal ions as 150 mg/L with 70% and higher removal rate in single adsorption. When binary metal adsorption is compared to single metal adsorption, the removal rates were notably decreased, as expected. Removal rates were higher than 75% when both initial metal concentrations were lower than 25 mg/L. Highest adsorption capacities for nickel and copper ion concentration in binary adsorption system was 1060 and 1010 mg/g, respectively. Based on obtained data, nickel removal was lower than copper removal both in single and binary adsorption system.

References

Arsenic and Boron Removals from Spring and Groundwater Samples in Boron Mining Regions of Turkey by Electrocoagulation and Ion-exchange processes

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Abstract

Borate mines in Bigadiç district in Turkey have the largest colemanite and ulexite deposits in the world. Boron (B) and arsenic (As) are two important contaminants determined in the spring and groundwater around the Bigadiç borate mines. Arsenic is the major pollutant and its concentrations range from 20 to 1250 μg/L in the groundwater. The concentrations of boron in the study area lie between 2 and 400 mg/L and the highest B concentrations are detected in this mine area. Therefore, the World Health Organization (WHO) allowed the maximum arsenic concentrations in drinking water is 10 μg/L. The WHO has provided a guideline for boron concentration in drinking water to be less than 2.4 mg/L because they are potentially hazardous to health and could have an adverse effect on skin and nervous system in humans. So, natural waters containing boron should be treated before providing safe drinking water into water supply system.

In this study, electrocoagulation (EC) process was used for removal of arsenic from waters since EC is capable of removing arsenic to trace levels and EC is simple in operation, compact treatment facility, cost-effective and no need to handle chemicals. Applied current and electrolysis time are important parameters influencing arsenic removal efficiency and operating cost. The removal efficiencies of As from spring and groundwater samples containing different arsenic concentrations of 36-1021 μg/L at 0.025-0.10 A and operating time of 1-60 min were achieved >97-99.9% at 2-16 min for Fe electrode (effluent concentrations of <10 μg/L). However, EC was not found to be successful for removal of B which was about 1-4.3%. Therefore, B in the samples after EC process was treated with ion-exchange resin (Amberlite IRA-743). Adsorption capacity of boron from water samples (5.9-333.1 mg B/L) was calculated as 0.30-58.73 mg B/g. The results from Bigadiç borate mines in spring and groundwater provided the required effluent concentration or removal efficiencies of arsenic and boron by the WHO using EC and ion-exchange processes.

Keywords: Arsenic contamination, spring and groundwater, electrocoagulation, Boron mining region

Introduction

Arsenic (As) originates in crystalline minerals in rocks containing sulphur and is often associated with pyrite (iron sulphide) and copper, gold, silver and other metal-rich ore rocks. However, arsenic is typically found along with boron minerals in the form of sulphur minerals such as realgar (AsS) and orpiment (AsS3) in Turkey (Helvaci and Alonso, 2000). Arsenic is one of the most important drinking water pollutants because of its carcinogenicity and toxicity.
Boron (B) has a positive effect on functioning of many organs but long-term consumption of water and food with increased boron content results in creation of problems with cardiovascular, coronary, nervous and reproductive systems. Excess of boron can be particularly dangerous for pregnant women as it increases the risk of birth pathology. High daily doses of boron cause testicular atrophy and degeneration (Wolska and Bryjak, 2013). In addition, boron concentrations >1 mg/L in irrigation water can cause plant damage (Polat et al., 2004). Therefore, drinking water standards for As and B suggested by the World Health Organization (WHO) are set as 10 μg/L and 2.4 mg/L, respectively (Wolska and Bryjak, 2013, WHO, 1996). The known borate reserves in Turkey are located in four main districts: Balıkesir-Bigadiç, Kütahya-Emet-Hisarcık, Eskisehir-Kırka, and Bursa-Kestelek (Helvaci and Alonso, 2000). Turkish production is controlled by the Eti Mine Cooperation, the national mining enterprise supplying most of the commercially traded tincal, ulexite, colemanite and borax from the borate mines (Onal and Burat, 2008; Helvaci and Orti, 1998). The Bigadiç borate deposits are among the largest colemanite and ulexite deposits in the world. As and boron pollutions were reported in surface and groundwaters in the areas of borate mining in Turkey (Gemici et al., 2008; Çolak et al., 2003). High As and B concentrations in groundwater are in part natural and related to leaching of the borate-bearing rocks of Neogene saline lake sediments. Therefore, As and B are two important contaminants in the spring waters and groundwater around the Bigadiç borate mines. As and B in these waters range from 33 to 911 μg As/L and from 0.05 to 640 mg B/L, respectively, and the greatest B concentration with 260 mg/L was detected at the open pit mines (Gemici et al., 2008). Simsek et al. (2003) indicated that the boron concentrations were unusually high in the groundwater, spring water and tap water (2-29 mg/L) and the agricultural products grown areas (10.24-67 mg/kg). Simsek et al. (2003) determined that the highest boron concentrations (2-29 mg/L) had regularly been measured in the town of Iskele in Bigadiç and its neighbourhood. Also, women from the boron-rich regions in Bigadiç mines had observed cytopathological findings because of the concentrations (1.2-20.75 mg/L) of boron in the drinking water consumed by the Bigadiç residents (Korkmaz et al., 2007). Sayli et al. (1998) investigated the relationship between elevated boron intake and fertility in the residents of villages with high levels of boron in their drinking water (0.03 to 29 mg/L at Bigadiç borate mines) (Gemici et al., 2008). Concentrations of As and B in spring water and groundwater for drinking and irrigation are greater than the safe levels. In addition, numerous cases of As and B pollutions in natural water sources around mining deposit, geothermal and coal fields in Western Anatolia of Turkey were reported in recent years. As and B concentrations in surface and groundwater are 0.5-562 μg As/L and 0.21-3.6 mg B/L for Kütahya-Simav (Gündüz et. al., 2010) and 0.7-170.1 μg As/L and 0.1-9.5 mg B/L for İzmir-Balçova Plains in geothermal fields (Aksoy et al., 2009), 10-10700 μg As/L and 300-500 μg As/L for İğde and Dulkadir villages of the Kütahya (Doğan and Doğan, 2007; Çöl and Çöl, 2004), and 70-7754 μg As/L and 0.2-4.4 mg B/L for Kütahya-Emet-Hisarcık (Çolak et al., 2003). Natural water sources where arsenic and boron pollutions take place are used mainly irrigation for lands, animal and humans. Consequently, natural waters from some regions in Western Anatolia of Turkey pose a potential threat to the community health related to high concentrations of As and B. Therefore, it may be necessary to treat spring and groundwater to remove these pollutants if As and B concentrations are higher than the set levels. Indeed, As and B in water are the most difficult components to remove using one water treatment process as compared to removal of other contaminants in water.
Various technologies are available for the removal of arsenic from contaminated water including coagulation using ferric and aluminium based salts, adsorption, lime softening, ion exchange, and membrane separation (Mondal et al., 2013). In recent years, electrocoagulation (EC) process has been shown to be a promising and alternative method for treatment of arsenic contaminated natural water samples due to considerable advantages of the process namely, higher removal efficiency, no pH adjustment, no chemical requirement for pre-oxidation of As(III) to As(V), simple in operation, compact treatment facility, and relatively cost-effective (Koby et al., 2015). Although, the removal efficiency of arsenic by the EC was obtained as high as 99% from surface and groundwater samples (Koby et al., 2015; Amrose et al., 2013; Parga et al., 2005), the methods commonly used in water treatment such as co-precipitation, coagulation, electrocoagulation, adsorption and membrane processes were not very effective in the case of boron compounds present (Wolska and Bryjak, 2013). The removal efficiency with reverse osmosis (RO) was achieved about 40-80% and over 90% in alkaline solutions (pH = 10-11) (Parsaei et al., 2011). But RO process is not effective because of the membrane cost, scaling and stability. Another method for removal of boron is co-precipitation through dilute boron solutions (1.6-0.16 mg/L) could be treated by efficiency of 90% using aluminium sulphate and calcium hydroxide. However, ion exchange is one of the most promising methods because it requires simple operating conditions and can be applied to low or high boron concentration. The technology commonly used for the removal of boron from aqueous solutions is ion-exchange process and commercial chelating resins as Amberlite IRA 743, Purolite S-108, and Diaion CRB 05 were useful for removal of boron in the range 93 and 98% (Darwish et al., 2015).

In this study, arsenic and boron removals in spring and groundwater from open-pit boron mines around Balikesir-Bigadiç were investigated with electrocoagulation and ion-exchange processes. Firstly, removal of arsenic from natural water samples in a batch EC reactor was achieved with iron (Fe) plate anodes. Effects of operating time and applied current on removal efficiency of arsenic were studied and results were analysed according to drinking water recommendation by WHO (<10 μg/L). Secondly, effluent of EC was treated with commercial resin (Amberlite IRA 743) for removal of boron and effect of resin dosage on B removal efficiency was investigated.

**Material and methods**

**Characterization of natural water samples**

Bigadiç deposits formed within Neogene perennial saline lake sediments (Gemici et al., 2008). The Turkish Borax Company has been operating mines in the Bigadiç borate deposit areas since 1976 and borate minerals are dominantly colemanite and ulexite. There are three main borate mines: namely Simav, Tülü and Acep borate open pits in the Bigadiç region and these open pits are 10 km from downtown Bigadic. Groundwater in borate deposit areas is located in the fractures of Neogene rocks, alternating terrestrial sediments and volcanic rocks. Generally, springs are found along the contact of the alternating beds of permeable and impermeable (clayey levels) units; these springs satisfy part of the water demand for drinking and agricultural purposes for the people in the villages around the study area. People live in villages and towns and around the mine region. The arsenic and boron contaminated waters are mostly observed.
in spring waters such as (SW: spring waters) SW-1: Küçük Spring Fountain, SW-2: Osmanca Village Spring Fountain, SW-3: İnce Memed Spring Fountain and SW-4: Cuma Spring Fountain spring in Iskele town (Korkmaz et al., 2007; Gemici et al., 2008), and samples from spring water in this study are taken as pointed in Figure 1. Therefore, some of the springs are abandoned and water is supplied by transportation from other water sources. However, some spring waters with relatively high arsenic and boron contents have continued to be used by the people living in these villages due to the inadequate supply of water. Moreover, samples are collected from a spring fountain (SW-5) near Simav boron open pit, and groundwater within Tülü and Acep open pits (groundwater, GW-1 and GW-2) (Figure 1). The climate characterized by arid, sunny summers and wet, cold winters in Bigadiç is transitive between the Mediterranean and Black Sea climate regions. Autumn is long and spring is short and rainy. The mean precipitation is around 570 mm. The yearly average temperature is 14.5 °C.

Figure 1. Map location of borate mine regions in Turkey and locations of water sample sites around Bigadiç borate area.

Water demands for drinking and agricultural purposes have been supplied mostly by springs, groundwater and surface waters for years. Groundwater from most of the springs is in contact with the borate mineral bearing rocks of the lower and upper borate zones. The dominant As and B in the groundwater are related to the geological setting in the area. Parameters such as pH, temperature, electrical conductivity (κ) and total dissolved solids (TDS) were measured in the field with portable devices. After making these measurements, the samples were filtered through 0.45 μm filter papers and preserved for analysis. Each sample was stored in two polyethylene bottles. One of them was acidified with HCl for cation analysis. The other was kept un-acidified for chloride, sulphate and alkalinity analyses. Samples stored at 4 °C for no more than 1 week were analysed in the Instrumental Analyses Laboratory of Environmental Engineering Department, Gebze Technical University. The results are presented in Table 1.
Table 1. Chemical analyses of natural water samples.

<table>
<thead>
<tr>
<th>Sample s</th>
<th>pH</th>
<th>K (μS/cm)</th>
<th>TDS (mg/L)</th>
<th>HCO₃⁻ (mg/L)</th>
<th>B (mg/L)</th>
<th>PO₄³⁻ (mg/L)</th>
<th>SO₄²⁻ (mg/L)</th>
<th>Cl⁻ (mg/L)</th>
<th>Mg (mg/L)</th>
<th>Ca (mg/L)</th>
<th>Si (mg/L)</th>
<th>As (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW-1</td>
<td>8.67</td>
<td>702</td>
<td>303</td>
<td>356</td>
<td>14.39</td>
<td>1.35</td>
<td>33</td>
<td>10</td>
<td>54.92</td>
<td>61.2</td>
<td>26.53</td>
<td>36.03</td>
</tr>
<tr>
<td>SW-2</td>
<td>8.62</td>
<td>904</td>
<td>387</td>
<td>444</td>
<td>6.16</td>
<td>1.16</td>
<td>23</td>
<td>11</td>
<td>70.06</td>
<td>81.2</td>
<td>30.05</td>
<td>113.5</td>
</tr>
<tr>
<td>SW-3</td>
<td>8.92</td>
<td>1004</td>
<td>431</td>
<td>440</td>
<td>27.38</td>
<td>1.52</td>
<td>30</td>
<td>9</td>
<td>74.74</td>
<td>79.6</td>
<td>28.64</td>
<td>185.9</td>
</tr>
<tr>
<td>SW-4</td>
<td>8.88</td>
<td>680</td>
<td>290</td>
<td>425</td>
<td>9.50</td>
<td>1.54</td>
<td>42</td>
<td>17</td>
<td>67.71</td>
<td>54.2</td>
<td>27.65</td>
<td>706.5</td>
</tr>
<tr>
<td>SW-5</td>
<td>8.72</td>
<td>1082</td>
<td>468</td>
<td>598</td>
<td>93.67</td>
<td>1.95</td>
<td>63</td>
<td>19</td>
<td>117.1</td>
<td>90.1</td>
<td>21.21</td>
<td>800.5</td>
</tr>
<tr>
<td>GW-1</td>
<td>9.24</td>
<td>1844</td>
<td>799</td>
<td>480</td>
<td>336.6</td>
<td>1.45</td>
<td>130</td>
<td>6.5</td>
<td>43.30</td>
<td>222.8</td>
<td>11.17</td>
<td>1020.5</td>
</tr>
<tr>
<td>GW-2</td>
<td>9.29</td>
<td>1084</td>
<td>466</td>
<td>328</td>
<td>226.7</td>
<td>0.99</td>
<td>520</td>
<td>6.3</td>
<td>14.76</td>
<td>188.1</td>
<td>11.59</td>
<td>300.5</td>
</tr>
</tbody>
</table>

SW-1: Küçükkınar Spring Fountain, SW-2: Osmanca Village Spring Fountain, SW-3: Cuma Spring Fountain, SW-4: İnce Memed Spring Fountain, SW-5: Simav Spring Fountain, GW-1: Acep Open Pit Mining Groundwater, GW-2: Tülü Open Pit Mining Groundwater.

Experimental set-ups and procedures

EC studies: The experimental set-up for the EC reactor was reported elsewhere (Kobya et al., 2011). The EC studies were carried out in a 1.0 L solution capacity in a batch glass reactor with a dimension of 12 cm × 11 cm × 11 cm at a constant temperature of 20 °C. The solution was constantly stirred at a rate of 400 rpm by means of a magnetic bar (Heidolp 3600 model) to reduce the mass transport over potential of the EC reactor. Four rectangular plate electrodes, two anodes and two cathodes of the same dimensions (5.0 cm × 7.3 cm × 0.3 cm) with purity of 99.5% were placed in the reactor. Total effective electrode area was 219 cm² and the spacing between the electrodes was 1 cm. The electrodes were placed into the reactor at monopolar parallel connection mode. The electrodes were connected to a digital DC power supply (Agilent 6675A model). During each experimental run, 0.85 L of spring or groundwater containing arsenic was placed into the EC reactor. Current was held constant at desired values for each run and the experiment was started. The samples at the different operating times taken from the EC reactor were filtered using a 0.45 μm membrane filter and metal concentrations were determined. At the end of the run, the electrodes were washed thoroughly with water to remove any solid residues on the surfaces, dried and reweighed. The sludge after the EC experiment was dried at 105 °C.

Ion-exchange studies: A commercial anion exchange resin, Amberlite IRA 743 supplied from Merck Darmstadt-Germany in this study was used (total capacity: 0.7 eq/L, harmonic mean size: 0.500-0.700 mm, shipping weight: 700 g/L, moisture holding capacity: 48 to 54%). Having Macro-porous polystyrene matrix on which N-methylglucamine functional group is attached makes this resin one of the most boron selective adsorbents. Therefore, sample treated by EC process was subject to filtration to continue boron removal with Amberlite IRA 743 resin. A series of batch ion-exchange tests were conducted to evaluate resin dosage. All the tests were done in capped volumetric flask (100 mL) by adding different resin dosages (0.025-3 g) and 50 mL spring or groundwater samples. Temperature was kept constant in a water bath with shaker. Shaking speed was 150 rpm. Adsorbent and solution mixtures were shaken 24 h. After adsorption samples were filtrated and boron in supernatants was analysed. The concentration
of boron was analysed using inductively coupled plasma optical emission spectrometer (ICP-OES).

**Analytical methods**

The chemical analyses of all water samples were carried out according to standard methods (APHA, 1998). Before and after EC for As and B and ion-exchange experiments for B were analysed in samples. Boron and arsenic concentrations of the solutions were measured using an inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer Optima 7000 DV model). ICP-OES detection limits were 0.1 μg/L for As and 0.05 mg/L for B. Total arsenic determination requires reducing using KI (10%) and ascorbic acid to convert As(V) to As(III) prior to the arsine formation step. In this study, the water sample (10 mL) was first mixed with 1 mL HCl (10%) and 1 mL of reducing agent (5% KI and 5% ascorbic acid), and then allowed to react for about 60 min at dark place to reduce As(V) to As(III). The concentrations of other cations and elements in the samples were determined by ICP-OES. Anions such as sulphate, chloride and phosphate in natural water samples were determined by an ion chromatography (Shimadzu HIC-20A). Alkalinity was determined by titration following accredited testing procedures. The pH and temperature of water samples were measured using a pH meter (Hach Lang HQ40d model) and the conductivity and TDS were determined with a conductivity meter (Mettler Toledo SG3 model). All the chemical reagents used were of analytical grade. The experiments were repeated twice. The experimental error was below 2% and the average data were reported in this study.

**Result and discussion**

**Arsenic removal by electrocoagulation**

Arsenic removals from natural water samples obtained from Bigadiç borax open pits and near surroundings were investigated with respect to applied currents and operating EC times. Results of the water samples illustrated in Table 1 are shown in Figure 2. Total As and B concentrations in İskele town, Bigadiç where one of spring water is Küçükpinar spring fountain (SW-1) were measured as 36.03 μg/L and 14.39 mg/L. People in town use water for daily needs and drinking purposes. The applied currents and operating times varied in the range of 0.025-0.10 A and 0-10 min in the EC process. As removal efficiency was carried out with different currents in the EC process in order to meet the WHO limit value (<10 μg/L). As removal efficiency needed for SW-1 was >72.3%. Therefore, the required EC times were 3 min (Cₐ = 7.6 μg/L) for 0.025 A, 2 min (Cₐ = 8.9 μg/L) for 0.05 A, and 2 min (Cₐ = 5.3 μg/L) for 0.10 A (Fig. 2(a)). Effluent pHₐ values at 10 min were 8.83 for 0.025 A, 8.91 for 0.05 A and 9.10 for 0.10 A.

B removal efficiencies at 0.025, 0.05, and 0.10 A were determined as 3.4, 3.9, and 4.6%, respectively. Energy and electrode consumptions for As removal efficiency of 72.3% were 0.00429 kWh/m³ and 0.00372 kg/m³ for 0.025 A, 0.00529 kWh/m³ and 0.00496 kg/m³ for 0.05 A, and 0.00917 kWh/m³ and 0.00992 kg/m³ for 0.10 A. Moreover, charge loading (q = i × tₑc) increased along with EC time but, minimum time required for removal of As at 0.025, 0.05 and 0.10 A was 10 min.
As and B concentrations in Osmanca Village Spring Fountain (SW-2) near Bigadiç-İskel town were 113.5 μg/L and 6.16 mg/L, respectively. Optimum effluent As concentrations were reduced from 113.5 μg/L to 8.3 μg/L for 0.025 A and from 113.5 μg/L to 4.6 μg/L for 0.05 A at t_{EC} = 8 min, and from 113.5 μg/L to 6.3 μg/L for 0.10 A at t_{EC} = 6 min (Figure 2(b)). Final pH values at 15 min for 0.025, 0.05 and 0.10 A were 8.71, 8.83 and 8.95, respectively. Charge loading, energy and electrode consumptions at these conditions were charge loading (q) = 12 C, 0.00733 kWh/m³ and 0.00992 kg/m³ for 0.025 A, q = 24 C, 0.0104 kWh/m³ and 0.0199 kg/m³ for 0.05 A and 36 C, 0.0131 kWh/m³ and 0.0298 kg/m³ for 0.05 A. As removal efficiency for SW-2 increased with increase in applied currents which led to decrease in operating time and increase in energy and electrode consumptions. B removal efficiencies at 15 min of EC time were found to be 4.2% for 0.025 A, 4.7% for 0.05 A and 5.8% for 0.10 A.

As removal efficiencies at 0.025, 0.05 and 0.10 A of applied currents for Cuma Spring Fountain in İskel town (initial concentrations of SW-3: 185.9 μg As/L and B = 27.38 mg B/L) were 95.21% at t_{EC} = 10 min, 97.5% at t_{EC} = 10 min, and 95.3% at t_{EC} = 6 min, respectively (Figure 3(a)). Effluent pH at 15 min were 9.02 for 0.025 A, 9.14 for 0.05 A and 9.21 for 0.10 A. According to the WHO limit value, required charge loading, energy and electrode consumptions were calculated as q = 15 C, 0.00917 kWh/m³, 0.0124 kg/m³ for 0.025 A; q = 30 C, 0.013 kW/m³ and 0.0248 kg/m³ for 0.05 A; and q = 36 C, 0.0131 kW/m³ and 0.0298 kg/m³, respectively. Effluent B concentrations for 0.025, 0.05 and 0.10 A at 20 min of EC time were measured as 26.2, 25.9, and 24.8 mg/L, respectively. According to the WHO limit value, required charge loading, energy and electrode consumptions were calculated as q = 15 C, 0.00917 kWh/m³, 0.0124 kg/m³ for 0.025 A; q = 30 C, 0.013 kW/m³ and 0.0248 kg/m³ for 0.05 A; and q = 36 C, 0.0131 kW/m³ and 0.0298 kg/m³, respectively. Effluent B concentrations for 0.025, 0.05 and 0.10 A at 20 min of EC time were measured as 26.2, 25.9, and 24.8 mg/L, respectively.

High As and B concentrations in SW-4 (Ince Memed Spring Fountain) used by residents in Bigadiç-İskel town were determined as 706.5 μg/L and 9.5 mg/L, respectively. Effluent As concentrations at 0.025, 0.05 and 0.10 A in the EC process were 8.9 μg/L at t_{EC} = 40 min, 7.4 μg/L at t_{EC} = 20 min, and 8.3 μg/L at t_{EC} = 15 min, respectively (Fig. 3(b)). Effluent B concentrations for 0.025, 0.05 and 0.10 A at 40 min were 9.1, 8.9 and 8.7 mg/L. final pH for 0.025, 0.05 and 0.10 A at 40 min were 8.93, 9.1 and 9.12, respectively. Required charge loadings at optimum EC times were calculated as 60, 60 and 90 C. Energy and electrode consumptions at these conditions were 0.0367 kWh/m³ and 0.0496 kg/m³ for 0.025 A; 0.0261 kWh/m³ and 0.0496 kg/m³ for 0.05 A; and 0.0327 kWh/m³ and 0.0744 kg/m³ for 0.10 A, respectively.
Figure 3. As removal efficiencies at different applied currents for SW-3 and SW-4 in the EC process.

The highest B (93.67 mg/L) and As (800.5 μg/L) concentrations were found in SW-5 (Simav spring fountain). Arsenic removal efficiencies for optimum EC times at 0.025, 0.05 and 0.10 A were 99.1% (Cf = 7.3 μg/L) at tEC = 40 min, 98.93% (Cf = 8.6 μg/L) at tEC = 20 min, and 99.1% (Cf = 7.4 μg/L) at tEC = 15 min, respectively (Figure 4(a)). pHf at 40 min for 0.025, 0.05 and 0.10 A were 8.81, 8.94 and 9.10, respectively. At 60 °C of charge loading, energy and electrode consumptions were 0.0367 kWh/m3 and 0.0496 kg/m3 for i = 0.025 A and 0.026 kWh/m3 and 0.0496 kg/m3 for i = 0.05 A. At i = 0.10 A and q = 90 C, energy and electrode consumptions were 0.0327 kWh/m3 and 0.0744 kg/m3.

Boron and arsenic concentrations in Acep (GW-1) and Tülü (GW-2) borate open pits were 1020.5 μg As/L and 336.6 mg B/L, and 300.5 μg As/L and 226.7 mg B/L (Table 1). B concentration is very high in these mines because boron minerals are in contact with in natural waters. At 0.025, 0.05 and 0.10 A, effluent As concentrations in the EC process were 7.2 μg/L at 60 min, 6.9 μg/L at 50 min and 7.1 μg/L at 30 min of EC time (Figure 4(b)). Effluent B concentrations for 0.025, 0.05 and 0.10 A at tEC = 60 min were obtained as 333.1, 330.3 and 297.4 mg/L, respectively. Energy and electrode consumptions were 0.0465 kWh/m3 and 0.0944 kg/m3 at q = 90 C for i = 0.025 A, 0.0530 kWh/m3 and 0.154 kg/m3 at q = 150 C for i = 0.05 A, and 0.0511 kWh/m3 and 0.179 kg/m3 at q = 180 C for i = 0.10 A, respectively. As applied current was increased, electrode and energy consumptions were increased but operating time was decreased. On the other hand, effluent pHf for 0.025, 0.05 and 0.10 A at 60 min were 9.8, 10.2 and 10.8, respectively. Dissolved amount of Fe anodes was increased with increase in pH since more Fe was dissolved at high pH. However, it was thought that the removals from groundwater were achieved with precipitation with Fe-arsenic ions and adsorption. Ferric ions generated by electrochemical oxidation of Fe electrode may form monomeric species and polymeric hydroxyl iron complexes depending on the pH of the aqueous medium, which have strong affinity for dispersed particles as well as counter ions to cause coagulation. In addition, arsenic is usually strongly adsorbed by iron oxides such as amorphous Fe(OH)3, hydrous ferric oxide (HFO) and goethite (FeOOH). Therefore, arsenic is removed by iron species either by compound formation or by surface complex adsorption or both (Kobya et al., 2011).

\[ 4Fe \rightarrow 4Fe^{2+} + 8e^- \]  \hspace{1cm} (1)

\[ Fe^{2+} \rightarrow Fe^{3+} + e^- \]  \hspace{1cm} (3)
\[ 2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- \]  \hspace{1cm} (3)

When introducing air (or oxygen) to the process, Fe\(^{2+}\) is oxidized rapidly in bulk solution:
\[ O_2(g) + 4Fe^{2+} + 2H_2O \rightarrow 4Fe^{3+} + 4OH^- \]  \hspace{1cm} (4)

The applied current forces OH\(^-\) ion migration towards the anode, thus favouring ferric hydroxide formation (Kobya et al., 2014; Kobya et al., 2011):
\[ Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3(s) \]  \hspace{1cm} (5)

The arsenic removal by co-precipitation results in that the OH\(^-\) positions in hydroxide are substituted by arsenic ions:
\[
\begin{align*}
2FeOOH{(s)} + H_2AsO_4^- & \rightarrow (FeO)_{2}HAsO_4^- + H_2O + OH^- \hspace{1cm} (6) \\
3FeOOH{(s)} + HAsO_4^{2-} & \rightarrow (FeO)_{3}AsO_4{(x)} + H_2O + 2OH^- \hspace{1cm} (7)
\end{align*}
\]

**Figure 4.** As removal efficiencies at different applied currents for SW-5 and GW-1 in the EC process.

Groundwater sample taken from Tülü boron open pit contained 300.5 μg/L of arsenic and 226.7 mg/L of boron (Table 1). Effluents As concentrations after the EC process were 8.2 μg/L at \( t_{EC} = 40 \) min for 0.025 A, 5.6 μg/L at 15 min for 0.05 A, and 7.8 μg/L at 10 min for 0.10 A (figure not depicted). In this case, energy and electrode consumptions were 0.0368 kWh/m\(^3\) and 0.0511 kg/m\(^3\) at \( q = 60 \) C for \( i = 0.025 \) A, 0.021 kWh/m\(^3\) and 0.036 kg/m\(^3\) at \( q = 45 \) C for \( i = 0.05 \) A, and 0.0205 kWh/m\(^3\) and 0.045 kg/m\(^3\) at \( q = 60 \) C for \( i = 0.10 \) A, respectively. Moreover, effluent pH\(_f\) for 0.025, 0.05 and 0.10 A at 40 min were 8.9, 8.6 and 8.5. Effluent B concentrations for 0.025, 0.05 and 0.10 A at the EC conditions were 223.2, 218.6, and 212 mg/L, respectively.

**Studies on boron removal by ion exchange**

As concentrations in the water samples were reduced to the required level set by the WHO (<10 μg/L) in the EC process using Fe plate anodes. The lowest energy and electrode consumptions from the above results were obtained at 0.025 A because values of the consumptions affected the operating cost of the EC process. After the filtration of samples (sludge from the EC) were treated for removal of B with Amberlite IRA 743 resin (0.025 g-1 g). B removal efficiencies for SW-1, SW-2, SW-3, SW-4, SW-5, GW-1 and GW-2 were 3.4, 4.2, 4.3, 4.2, 3.8, 1.04, and 264
As seen from the results that EC process was not successful to remove B from the sample efficiently (Table 1). Other important point is pH value of natural waters containing B. During the EC process effluents pH values were noticed to increase and this was an advantage to remove B from the sample using ion-exchange process using Amberlite IRA 743 resin at pH 8-11 which was the recommended values of pH range (Darwish et al., 2008). Therefore, no pH adjustments for removal of B were made after effluents collected from the EC process. Effluents pH values in the EC process were found to be 8-10. Effluents B concentrations ($C_f$, mg B/L) and adsorption capacity ($q_e$, mg B/g resin) at different resin dosages are presented in Tables 2 and Figure 5. As the resin dosages were increased, concentrations of $C_f$ were decreased but amount of B adsorbed per resin dose (g) was observed to decrease (Tables 2 and Figure 5). In addition, boron absorbed decreased as the initial boron concentration increased in water samples. Some literature results were reported with use of the resin in the following studies. Darwish et al. (2015) investigated boron removal by Amberlite IRA743, and adsorption capacities were 3.67 and 5.41 mg/g for feed solution with initial boron concentrations of 1.5 and 5.0 g/L at the optimum conditions (the resin dosage= 0.4 g/L, pH = 8, T = 25 °C, and ion-exchange time: 120 min, respectively. Boron adsorption capacity at different experimental conditions was calculated as 6.7 mg B/g resin by Xu and Jiang (2008), and 7.5 mg B/g resin by Wei et al., (2011). The pH dependence of boron uptake was interpreted by taking into account the dissociation process of $B(OH)_3$ in aqueous solutions and formation of bidentate complex of borate ion with two N-methyl-D-glucamine groups of the resin. The resin's hydroxyl groups had higher affinity for $B(OH)_4^-$ ions comparing with $B(OH)_3$ species (Darwish et al., 2015). Boric acid at a pH lower than 7 is not dissociated as $H_3BO_3$ or $B(OH)_3$, but boron occurs as dissociated borate $B(OH)_4^-$. Therefore, many studies reported for removal of boron was optimised at pH 9-9.5.

**Table 2.** Results of boron removal for spring waters by Amberlite IRA 743 at different resin dosages.

<table>
<thead>
<tr>
<th>$w_s$ (g)</th>
<th>SW-1</th>
<th>SW-2</th>
<th>SW-3</th>
<th>SW-4</th>
<th>SW-5</th>
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<tr>
<td>$C_f$ (mg/L)</td>
<td>$q_e$ (mg/g)</td>
<td>$C_f$ (mg/L)</td>
<td>$q_e$ (mg/g)</td>
<td>$C_f$ (mg/L)</td>
<td>$q_e$ (mg/g)</td>
</tr>
<tr>
<td>0</td>
<td>13.87</td>
<td>0</td>
<td>5.9</td>
<td>0</td>
<td>26.2</td>
</tr>
<tr>
<td>0.025</td>
<td>6.32</td>
<td>15.1</td>
<td>1.3</td>
<td>9.2</td>
<td>8.1</td>
</tr>
<tr>
<td>0.050</td>
<td>2.4</td>
<td>11.47</td>
<td>0.2</td>
<td>5.7</td>
<td>2.2</td>
</tr>
<tr>
<td>0.075</td>
<td>0.35</td>
<td>9.01</td>
<td>0.01</td>
<td>3.9</td>
<td>0.4</td>
</tr>
<tr>
<td>0.100</td>
<td>0.04</td>
<td>6.39</td>
<td>0.001</td>
<td>2.9</td>
<td>0.1</td>
</tr>
<tr>
<td>0.250</td>
<td>0.01</td>
<td>2.77</td>
<td>0.001</td>
<td>1.2</td>
<td>0.001</td>
</tr>
<tr>
<td>0.500</td>
<td>0</td>
<td>1.39</td>
<td>0</td>
<td>0.59</td>
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<td>0</td>
<td>0.69</td>
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</tbody>
</table>
Conclusions

In this study, spring and groundwater samples contain As and B from Bigadiç boron mine areas were treated with EC process using Fe plate anodes. Effects of applied currents (0.025-0.1 A) and operating time (0-60 min) were evaluated for the removal in the EC process. The arsenic removal efficiency was determined with reaching the effluent concentration set by the WHO. As the operating time and current increased, the removal efficiency of As was increased. Especially, operating time was decreased with increasing the current density in the EC process. The operating time was also increased with increasing concentration of As in water samples. However, removal efficiencies of B in the EC process were not successful which were in the range of 1.0-4.3%. Final pH values were increased during the EC process which helped to increase the removal efficiency of B when the effluent was treated with ion exchange process since commercial boron removal resins are effective at pH 8-11. When the samples were filtrated after the EC process, boron in the water samples was removed with Amberlite IRA 743 resin at dosages 0.025-3 g in a batch process. This gave a removal efficiency of 99-100% for B in the spring and groundwater samples. As effluent B concentration of 1 mg/L was considered, B removal capacities of resin were found to be 0.24-7.4 mg B/g resin. As a results, the best processes for removals of As and B from natural waters in the boron mining regions were performed with EC process using Fe plate electrodes for As and ion exchange for B.

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Treatment of HDPE Plastic Washing Wastewater by Physicochemical Methods

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**ABSTRACT**

HDPE (High Density Polyethylene) plastic washing wastewater contains high concentrations of oil-grease, turbidity, COD (Chemical Oxygen Demand), BOD (Biochemical Oxygen Demand) and SS (Suspended Solids) that lead to an increase in the pollution load of wastewater treatment plant. Direct discharge of these wastewaters into the environment will have considerable adverse effects. In this study, a flocculant (SPS) was synthesized from waste Polystyrene (PS) by sulfonation, with cyclohexane, H₂SO₄, P₂O₅ modification. The produced flocculant was used in coagulation-flocculation treatment of HDPE plastic washing wastewater. The treatment efficiency was investigated with Jar-test experiments and compared to conventional coagulation-flocculation applications. Turbidity, oil-grease, COD and SS analyses were performed at the supernatant. Effects of pH were studied at pH 3-13 interval. Alum and FeCl₃ were used as conventional coagulants at 15-1000 mg/L dosages. The synthesized SPS and polyelectrolyte (PE) were used as flocculants at between 5-50 mg/L dosage. At the original pH of the wastewater 13±1, 1000 mg/L Alum+5 mg/L SPS resulted in 92% turbidity, 59% oil-grease, 93% COD and 76% SS removals, while for 1000 mg/L Alum+5 mg/L PE, they were 74%, 64%, 83% and 84%, respectively. These efficiencies were closer to each other when SPS and PE were used together with FeCl₃. At pH 13±1, the removal of turbidity, oil-grease, COD and SS were 96%, 50%, 90% and 85%, respectively for 1000 mg/L FeCl₃+10 mg/L SPS while they were 97%, 56%, 90% and 79%, respectively, for 1000 mg/L FeCl₃+10 mg/L PE. The produced SPS resulted in higher and/or close performances with PE.

**Keywords:** Coagulation-flocculation, HDPE, plastic washing wastewater, waste PS sulfonation, BOD, COD, Oil-grease, SS, Turbidity.

1. **INTRODUCTION**

Plastics are produced from petroleum derivatives and are composed primarily of hydrocarbons but also contain additives such as antioxidants, colorants, and other stabilizers. They have become an inseparable and integral part of our lives. The amount of plastics consumed annually has been growing steadily. Its low density, strength, userfriendly designs, fabrication capabilities, long life, light weight, and low cost are the factors behind such phenomenal growth. Plastics have been used in packaging, automotive and industrial applications, medical delivery systems, artificial implants, other healthcare applications, water desalination, land/soil
conservation, flood prevention, preservation and distribution of food, housing, communication materials, security systems, and other uses (Siddique et al., 2008).

According to 2013 Annual Report of the European Association of Plastics Manufacturers plastic production in 2012 amounted to 57 M tonnes in Europe and 288 M tonnes worldwide. Recycling (both mechanical and chemical) is the preferred option for waste plastic, as the product shelf life is increased. Nevertheless, less than 25% of the 25.1 M tonnes of waste plastic generated in Europe in 2011 was suitable for recycling, which is due to the production of composites and specially designed plastics, the use of new methods that improve the mechanical and superficial properties of the plastics, and the high cost of separation processes (Aguado et al., 2014).

HDPE is the third largest commodity plastic material in the world, after polyvinyl chloride and polypropylene in terms of volume. The demand for HDPE has increased 4.4% a year to 31.3 million MT in 2009. The increased demand and production of waste HDPE has led to the accumulation of large amount of its waste in the final waste stream due to its low useful life. Recycling of plastics already occurs on a wide scale (Kumar et al., 2013).

In order to be able to increase the quality of recycling processes of HDPE plastic wastes and of recycled plastic material, washing process is performed on plastics. In case residuals of product within HDPE plastic wastes are not collected separately from contamination coming from its package and other wastes, the fact that other organic contaminants cover significantly decreases the quality of waste material which is recovered. That’s why, by washing contaminated wastes, increasing the quality of plastic which is recovered can be provided. As a result of caustic washing process, wastewater with high pH is discharged into sewage without treatment in most of places.

The application of coagulation and flocculation is necessary for the removal of colloidal particles. Adding coagulants (such as aluminium or ferric salts) to the wastewater creates a chemical reaction in which the repulsive electrical charges surrounding colloidal particles are neutralized, allowing the particles to stick together creating clumps or flocs. Flocculants are then used to facilitate the agglomeration and decantation. Most common flocculants consist of polyelectrolytes such as derivatives of polyacrylamide and polystyrene. Polystyrene is a plastic which has been extensively used in packaging. Various investigations have adopted chemical recycling of waste polystyrene into the corresponding monomers or hydrocarbons. However, the process is not efficient because the cost of hydrocarbons and monomers is low compared to that obtained by recycling. Therefore, it is useful to find an efficient technique to recycle waste polystyrene. A polystyrene recycling method has been developed which seems to be more efficient (Vink, 1981). The goal of this process is to convert polymer waste into a functional polymer with a new application and added value. It is well-known that the sulfonation of polystyrene allows obtaining interesting products such as cationic exchanger resin, polyelectrolyte and fuel cell membranes (Bekri-Abbes et al, 2007).

In this study, in order to minimize the environmental impact of high amount of contaminated wastewater which is obtained from HDPE washing processes, being able to be increased with the coagulation/flocculation is investigated. The study is based on the sulfonation of waste polystyrene to produce a polymeric flocculant and to use it for the removal of turbidity, COD,
BOD, oil-grease and SS from wastewater. In this way, both recycling plastic waste and decreasing the weight falling to urban wastewater treatment facility are contributed.

2. MATERIAL AND METHOD

2.1. Waste Plastic Washing

Washing of HDPE waste which is crushed 80 mm is performed in three steps. In the first step, after HDPE in 42% of NaOH is boiled at 90°C for 10 minutes, wastewater is obtained by treatment wastes (Santos, 2005). In the second and third steps, plastics obtained from this first step are boiled with tap water at 90°C for 10 minutes for rinsing. Waste plastic is left to dry. In the end of washing and two rinsing processes, plastic washing wastewater is obtained. Characterization of this HDPE washing wastewater is given in Table 1. The fact that such substances as detergents in HDPE containers are the most important reasons why COD value is high. Because washing process is performed with very concentrated caustic solution, the pH and Na values are high. While any considerable metal contamination is not observed in wastewater, it is seen that alkali metals present.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>HDPE washing wastewater</th>
</tr>
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<tbody>
<tr>
<td>BODs (mg/L)</td>
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</tr>
<tr>
<td>COD (mg/L)</td>
<td>3540</td>
</tr>
<tr>
<td>SS (mg/L)</td>
<td>1680</td>
</tr>
<tr>
<td>Oil-Grease (mg/L)</td>
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</tr>
<tr>
<td>Turbidity (NTU)</td>
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</tr>
<tr>
<td>Pb (mg/L)</td>
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</tr>
<tr>
<td>Cd (mg/L)</td>
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</tr>
<tr>
<td>Fe (mg/L)</td>
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<td>Mn (mg/L)</td>
<td>0.13</td>
</tr>
<tr>
<td>Na (mg/L)</td>
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<tr>
<td>S (mg/L)</td>
<td>106.95</td>
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<tr>
<td>Mg (mg/L)</td>
<td>2.27</td>
</tr>
<tr>
<td>K (mg/L)</td>
<td>6.27</td>
</tr>
<tr>
<td>Ca (mg/L)</td>
<td>33.50</td>
</tr>
</tbody>
</table>
2.2. Sulfonated PS (SPS) Synthesis

Sulphonated PS flocculent, which is used in the study of coagulation-flocculation, is obtained by the method of Vink (Vink, 1981). 1.5 g of crushed waste is dissolved in 75 mL cyclohexane. P₂O₅ is added to H₂SO₄ and dissolved in a separate erlenmeyer. By mixing the two solutions and keeping temperature at 40°C, the solution is waited for an hour. In separating funnel, polymer material is subsided as adhesive and yellow and Cyclohexane (supernatant), Polyacid (PSSH) (phase in middle), acidic solution and the phase containing P₂O₅ (sub-phase) are composed. Sub-phase is filtered in separating funnel. 150 mL of distilled water is slowly added to the mixture of supernatant polymer and cyclohexane and mixed. Cyclohexane is separated. pH of the liquid including polymer is adjusted to basic media with NaOH and powdery SPS flocculent is obtained by making the mixture dried at 40°C for a day.

2.3 Treatment with coagulation-flocculation

Coagulation-flocculation studies were performed with Jar-test. Alum and FeCl₃ as coagulant agent and PE and synthesized SPS as flocculent agent were used. The coagulant doses of 15, 50, 100, 1000 mg/L and the flocculent doses of 5, 10, 20, 40 and 50 mg/L were studied. Coagulant agent was added into erlenmeyer containing 250 mL wastewater and waited for sedimentation after a quick mixing in 125 rpm for 90 seconds and a slow mixing in 25 rpm for 15 minutes. After 1 hour sedimentation, analyses of turbidity and other parameters (BOD, COD, SS and Oil-Grease) were performed in supernatant of the samples. Based upon findings, the most efficient coagulant dose was determined and experiments were performed in different flocculent doses by fixing this value. After two most efficient flocculent doses were both determined, different pH studies in these doses were performed in natural pH value of raw wastewater and four different pH values (3, 5, 7, 9).

3. RESULTS AND DISCUSSION

3.1 Effects of Coagulants and Flocculants Dose on the Treatment of HDPE Washing Wastewater

Change in turbidity with Alum and FeCl₃ doses is given in Figure 1. In fact, it is provided that turbidity is removed at a rate of 70% approximately since the lowest doses studied and the increase in efficiency is observed at a very low level as the dose increases after this value. It is accepted that the efficiency of removal much increases and the best efficiency is in the doses of 1000 mg/L Alum and FeCl₃.

| Si (mg/L) | 8.81 |
| P (mg/L) | 7.01 |
Figure 1. Change of turbidity with Alum and FeCl₃ dose

From Figure 2a, Alum+5 mg/L and 20 mg/L SPS, Alum+5 mg/L and 40 mg/L PE, FeCl₃+10 mg/L and 20 mg/L SPS and FeCl₃+10 mg/L and 50 mg/L PE are determined as the two most efficient flocculent doses. Turbidity removal efficiencies are 92% for Alum+5 mg/L SPS, 74% for Alum+5 mg/L PE, 96% for FeCl₃+10 mg/L SPS and 97% for FeCl₃+10 mg/L PE. SPS flocculent with FeCl₃ are more efficient, similar results to PE or higher efficiency (93-97%) are obtained.

Removal of SS is provided in the dose of Alum+5 mg/L SPS at a rate of 76%, in the dose of Alum+5 mg/L PE at a rate of 83%, in the dose of FeCl₃+10 mg/L SPS at a rate of 86%, in the dose of FeCl₃+10 mg/L PE at a rate of 79%. It is seen that the difference of coagulant and flocculent doses does not have any impacts on removal of SS (Figure 2b). At these coagulant and flocculent doses, oil-grease removal efficiencies are 60%, 64%, 50% and 56%, respectively (Figure 2c). It is observed that the results with Alum+SPS/PE are more efficient in removal of oil-grease in HDPE washing wastewater.

Change of COD concentrations of the samples is shown in Figure 2d. It is determined that removal of KOI is good in both coagulant and flocculent doses and varies between 84-94%.
BOD removals are high in the combinations of Alum+SPS, Alum+PE ve FeCl$_3$+SPS, FeCl$_3$+PE for HDPE plastic washing wastewater (Table 2). It is observed that SPS flocculent is effective in removal of BOD similar to PE in the doses of 5-10 mg/L and gives better results together with Alum.

Table 2. BOD change with SPS ve PE dose of HDPE washing wastewater treatment

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Flocculant</th>
<th>BOD (mg/L)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw wastewater</td>
<td>-</td>
<td>-</td>
<td>1790</td>
</tr>
<tr>
<td>Alum+SPS</td>
<td>1000</td>
<td>5</td>
<td>330</td>
</tr>
<tr>
<td>Alum+PE</td>
<td>1000</td>
<td>5</td>
<td>110</td>
</tr>
<tr>
<td>FeCl$_3$+SPS</td>
<td>1000</td>
<td>10</td>
<td>210</td>
</tr>
<tr>
<td>FeCl$_3$+PE</td>
<td>1000</td>
<td>10</td>
<td>390</td>
</tr>
</tbody>
</table>

3.2. Effect of pH on Treatment of HDPE Washing Wastewater

In Figure 3a, the change of turbidity with pH values by using Alum, FeCl$_3$ coagulant and SPS, PE flocculent doses are indicated. It is determined that the most efficient removal is in the pH value of 3 in the combinations of Alum+SPS and Alum+PE (Figure 3a). The efficiency of removal of turbidity is observed for Alum+5 mg/L SPS with the pH value of 3 at a rate of 81% and for Alum+5 mg/L PE at a rate of 78%. As pH increases, the turbidity removal efficiency decreases. Aluminum hydroxide precipitates are not dissolved in the pH interval (3-4 and 4.5-8, in which precipitation starts. In treatment of water, it is determined that the most efficient treatment can relatively be performed in the pH range between 4.5 and 8 for Alum in general (Reynolds, 1995). This information acknowledges that the most efficient results are obtained in the pH between 3 and 5 with Alum. However, the efficiency of turbidity removal in the pH 7 and 9 was between 50% and 66%.
Figure 3. (a) Turbidity (b) SS (c) Oil-grease (d) COD changes with pH (1000 mg/L Alum+5 mg/L SPS, 1000 mg/L Alum+5 mg/L PE; 1000 mg/L FeCl$_3$+10 mg/L SPS, 1000 mg/L FeCl$_3$+10 mg/L PE)
A better efficiency is provided in FeCl₃+SPS in the pH value of 7 compared to other pH values (Figure 3a). For the pH value of 7, the efficiency of removal is provided with FeCl₃+10 mg/L SPS at a rate of 81% and with FeCl₃+10 mg/L PE at a rate of 79%. Between pH 3 and 5, efficiency decreases. The pH interval, hydroxide sediment is not dissolved relatively for FeCl₃, is between 4 and 12 (Reynolds, 1995). It was determined that the most suitable pH values are 7 and 9 with FeCl₃ in HDPE washing wastewater.

The most efficient SS removals were observed with Alum+SPS and Alum+PE in the pH value of 3 (Figure 3b). It provides 78% SS removal efficiency with Alum+5 mg/L SPS at pH 3 while 82% with Alum+5 mg/L PE. Changes in pH do not have any considerable impacts on SS removal efficiency in case of alum coagulant. However, the efficiencies decreased with FeCl₃. For FeCl₃+10 mg/L SPS 61% and in the dose of FeCl₃+10 mg/L PE 69% SS removal could be achieved at pH 7. The fact that FeCl₃ coagulant has such a large field of study like between pH 4 and 12 is concluded with the similarity of change in SS concentration between pH 3 and 9 (Figure 3b).

SPS flocculent is negatively affected by changes in pH in removal of oil-grease and its efficiency decreases (Figure 3c). However, removal is provided with Alum+PE between 54% and 63% at different pH values. It is determined that a more efficient removal is provided in SPS flocculent between pH 3 and 9 compared to PE for the oil-grease (Figure 3c). It is generally observed that SPS and PE flocculants are not as effective as other parameters (COD, BOD, SS and turbidity) in removal of oil-grease in HDPE washing wastewater.

In the treatment of COD, the efficiency of Alum+SPS flocculent decreases little compared to raw wastewater’s original pH value (pH 13±1). In the dose of Alum+5 mg/L SPS, COD removal varies between 66% and 84%. This situation changed to 90% for the dose of Alum+5mg/L PE and efficiency increases in pH 7-9 (Figure 3d). In pH 7, the COD removal efficiency with the dose of FeCl₃+10 mg/L SPS was at a rate of 86% and in the dose of FeCl₃+10 mg/L PE was at a rate of 61%. The efficiency of treatment of FeCl₃+PE COD decreases from 90% to 52% at pH 3 with changing pH of plastic wastewater. SPS flocculent provides a better removal compared to PE in COD removal at different pH values (Figure 3d).

BOD concentrations under different pH conditions are shown in Table 3. High efficiencies are obtained for each pH in the studies performed between pH 3 and 9 in the doses of Alum+5 mg/L SPS and Alum+5 mg/L PE. However, in the studies performed with FeCl₃+SPS and FeCl₃+PE, the BOD removal efficiency is higher than with Alum. It is concluded that removal of BOD shows a little difference in change of pH in HDPE washing wastewater and SPS flocculent provides a better removal compared to PE.
<table>
<thead>
<tr>
<th>Coagulant dose (mg/L)</th>
<th>Flocculant dose (mg/L)</th>
<th>BOD (mg/L)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw wastewater</td>
<td>-</td>
<td>1790</td>
<td></td>
</tr>
<tr>
<td>pH 3 Alum+SPS</td>
<td>1000</td>
<td>280</td>
<td>84</td>
</tr>
<tr>
<td>pH 5 Alum+SPS</td>
<td>1000</td>
<td>155</td>
<td>91</td>
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<tr>
<td>pH 7 Alum+SPS</td>
<td>1000</td>
<td>210</td>
<td>88</td>
</tr>
<tr>
<td>pH 9 Alum+SPS</td>
<td>1000</td>
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<td>86</td>
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<td>96</td>
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<tr>
<td>pH 9 FeCl₃+PE</td>
<td>1000</td>
<td>30</td>
<td>98</td>
</tr>
</tbody>
</table>

### 4. CONCLUSION

In the original pH (13±1) of HDPE washing wastewater, data about turbidity, SS, oil-grease and COD in supernatant as a result of treatment with the combinations of Alum+SPS, Alum+PE, FeCl₃+SPS and FeCl₃+PE suggests a better removal compared to those obtained in pH 3, 5, 7 and 9 while in BOD removal, the pH 3, 5, 7 and 9 are more efficient. In the treatment of HDPE wastewater, optimal coagulant, flocculant dose and pH are respectively determined as 1000 mg/L FeCl₃, 10 mg/L SPS dose and natural pH (13±1) (96%). In these conditions, the turbidity value of 1079 NTU of raw wastewater decreases to 45 NTU. FeCl₃ coagulant is more efficient than Alum at the original pH of raw water. In SPS flocculent, similar results to PE and sometimes more efficient results are obtained.
The highest performances on the parameter basis were obtained at different chemical and pH combinations. 86% SS removal efficiency is obtained in the dose of 1000 mg/L FeCl$_3$+10 mg/L SPS at original pH; 64% oil-grease efficiency is obtained in the dose of 1000 mg/L Alum+5 mg/L PE at original pH; with 1000 mg/L Alum+5 mg/L SPS at original pH, COD was reduced from to 236 mg/L (93%). For the BOD removal from 1790 mg/L to 30 mg/L (98%) the dose of 1000 mg/L FeCl$_3$+10 mg/L PE and pH9 were optimal conditions. Since COD/BOD>3 this shows that HDPE washing wastewater was somehow non-biodegradable and biological treatment is difficult.

Consequently, it is presented in this study that sulfonated PS flocculent, which is obtained from waste PS, can be used in chemical treatment. It is determined that SPS flocculent gives similar results to PE or better results in removal of turbidity, SS, COD, BOD and oil-grease from HDPE washing wastewater.

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INDEX

Ozonation for the Removal of Bisphenol-A from Aqueous Solutions ......................................................... 1
M. Mutseyekwa, S. Doğan, S. Pırşalıoğlu ................................................................. 1
Continuous versus Batch Contacting for Nutrient Recovery from Human Urine upon Processing with Clinoptilolite I: Surface Capacities and Operation Times ........................................ 7
A. D. Allar Emek, B. Beler Baykal ................................................................. 7
Simultaneous municipal waste-activated sludge stabilization and direct power generation by a novel reactor named AMFD ........................................ 13
H. Rasouli Sadabad, G. Badalians Gholikandi, Sh. Karami, H. Rasouli Sadabad, H. Masihi ........................................ 19
Heavy metals removal from waste-activated sludge employing Fered-Fenton electrochemical advanced oxidation technology with the aim of agricultural land application ........................................ 19
G. Badalians Gholikandi, Sh. Karami, H. Rasouli Sadabad, H. Masihi ........................................ 19
Fered-Fenton Electrochemical Advanced Oxidation Process for Waste-activated Sludge Stabilization and Reuse: Macronutrients Preservation and Microbial Inactivation ........................................ 26
Gagik Badalians Gholikandi, Shafieh Karami, Nazanin Zakizadeh, Hamidreza Masihi ........................................ 26
Investigation of Electro-Chemical Peroxidation (ECP) Process for Waste-activated Sludge Stabilization with the Aim of Agricultural Land Application ........................................ 33
Biogas Production from Hydrocarbon and Lipid-Spent Microalgae and Wastewater Sludge Mixtures ................................................................. 39
A. Shanableh, N. Adam ................................................................. 39
Effect of Inorganic Salt Solutions on Index Properties of Natural Liner Materials ........................................ 48
Gamze Varank, Ahmet Demir, Senem Yazici Guvenc, Sukru Ozcoban ........................................ 48
Physico-Chemical, Mineralogical and Geotechnical Investigations of Natural Liner Materials 54
Gamze Varank, Ahmet Demir, Senem Yazici Guvenc, Sukru Ozcoban ........................................ 54
Reduction and Biogas Recovery during Anaerobic Digestion of the X-Ray Contrast Agent Iopamidol ................................................................. 60
C. Yangin-Gomec, T. Sapmaz, S. Khoei, I. Arslan-Alaton, T. Olmez-Hanci ........................................ 60
Enhanced Degradation of Micropollutants by Zero Valent Aluminum Activated Persulfate: Assessment of Toxicity and Genotoxic Activity ................................................................. 66
T. Olmez-Hanci, I. Arslan-Alaton, M. Doğan, S. Khoei, H. Fakhri, G. Korkmaz ........................................ 66
Zero-Valent Aluminum-Mediated Degradation of Bisphenol A in the Presence of Common Oxidants ................................................................. 73
I. Arslan-Alaton, T. Olmez-Hanci, M. Doğan, T. Ozturk ................................................................. 73
The Role of Energy Consumption in Optimized Operation of Electrochemical Advanced Oxidation Processes: Fered-Fenton Reactor ................................................................. 79

278
Investigation of Variation of the Recyclable Solid Waste Amounts in Küçükçekmece District of Istanbul .................................................................................................................................................................................. 224

E. Elmaslar Özbaş*, S. Yiğit Hunce, H. K. Özcan, A. Öngen, S. Gazi .......................................................... 224

Heterogenous Photocatalytic Treatment of Synthetic and Real Grey Water Samples for Reuse Evaluation ............................................................................................................................................................................. 230

C. Kepoglu*, C.B. Özkal, S. Meriç Pagano* ........................................................................................................... 230

Assessment of thin-film photocatalysis inactivation of different bacteria strains and variation in antibiotic resistance behaviour .................................................................................................................................................................................. 237

C.B. Özkal*, D. Venieri, S. Meric ......................................................................................................................... 237

Wastewater Reuse Potential of Paint Operations in an Oven Manufacturing Plant ........................................... 244

E. Gümüşlu, Guçlu Insel, Tugba Olmez-Hancı, Fatos Germirli Babuna, Didem Okutman Tas, Emine Cokgor, Nilay Sayı Uçar, Goksin Ozyıldız, Gulten Yuksek, Nadir Dizge, Derya Firat Ertem, ÖkmenYıldırım, Ozge Erturan, Betul Kircı ................................................................................................................................. 244

Single and Binary Adsorption of Copper and Nickel Metal Ions on Nano Zero Valant Iron (nZVI) ................................................................................................................................................................................. 250


Arsenic and Boron Removals from Spring and Groundwater Samples in Boron Mining Regions of Turkey by Electrocoagulation and Ion-exchange processes .......................................................................................................................................................................................... 256

M. Kobya, M.S. Öncel, E. Demirbaş ..................................................................................................................... 256

Treatment of HDPE Plastic Washing Wastewater by Physicochemical Methods ........................................ 268

Nihan Canan İskendera, Esra Yela ..................................................................................................................... 268