Preface

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

The organizers would like to express their thanks to the keynote speakers for their excellent presentations. Special thanks should also be addressed to the members of the Scientific Committee. Moreover, we are very grateful to the members of the Organizing Committee as well as to our Sponsors who made the R&R, 2018 Conference a great success. Finally, we thank all participants without whom the R&R, 2018 Conference would not have been possible.

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

Hoşçakalın,

October 2018, Istanbul

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Effect of Landfill Leachate on Geotechnical Properties of Kaolinite Mixed with Additive Materials

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

Abstract

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

1. Introduction

Landfill leachates containing a large number of contaminants have been identified as one of the major threats to groundwater resources (US EPA, 1984; Fatta et al., 1999). The impact of landfill leachate on the surface and groundwater has given rise to a number of studies in recent years (Flyhammer, 1995; De Rosa et al., 1996; Christensen et al., 1998; Looser et al., 1999; Abu-Rukah and Kofahi, 2001; Saarela, 2003). The liner system is one of the most important elements of a modern engineered landfill. Compacted clay liners are the main components of composite liner systems consisting of a geomembrane overlaying a compacted soil liner or a geosynthetic clay liner. The clays are exposed to various chemical, biological and physical reactions occurring in the landfill body and affected by the resulting leachate. It is well known that the mechanical and hydraulic behaviour of clay soils can be strongly affected by the clay–leachate interaction (Yilmaz et al., 2008).

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

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

To represent leachate interaction with clay liner, salt solutions were used in experimental studies carried out to evaluate leachate effect of engineering properties of liner materials. Based on experimental studies it is concluded that both the liquid limit and the plastic limit of CL clay increased when salt solution concentrations were increased. This increase in consistency limits could be attributed to dispersion and deflocculation of the clay particles when the clay interacted with chemicals (Rao and Mathew 1995; Arasan and Yetimoglu, 2008). Additionally, salt solutions might cause to form new swelling compounds increasing the liquid limit of CL clay (Sivapullaiah and Manju, 2006). 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; Acar and Olivieri, 1990; Edil et al., 1991; Shackelford, 1994; 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 pariticles (nonswellng) 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 Mg$^{2+}$, Ca$^{2+}$, 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 (Arasan and 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. Several researchers have reported that chemical solutions at low concentrations are more effective than at high concentrations for CH clays (Alawaji, 1999; Jo et al., 2001).

Some additive materials can be used to improve the geotechnical properties of clay liners for interaction with fluid. The additive materials can limit the change in consistency limits before and after being exposed to the fluid. Cement addition is often used as a method to improve the strength and compressibility characteristics of materials (Balasubramaniam et al., 1998; O'Rourke et al., 1998; Schaefer et al., 1997; Chew et al., 2004). Cement addition
produces primary and secondary cementatious compounds in the clay–cement matrix improving the properties (Lorenzo and Bergado, 2006). The primary cementation compounds are formed by a hydration reaction and comprised of hydrated calcium silicates (C\text{2}SH\text{x}, C\text{3}S2H\text{x}), calcium aluminates (C\text{3}AH\text{x}, C\text{4}AH\text{x}), and hydrated lime Ca (OH): (Bergado et al., 1996). A secondary pozzolanic reaction between the hydrated lime and the silica and alumina from the clay minerals leads to the formation of additional calcium silicate hydrates and calcium aluminate hydrates (Chew et al., 2004). This reaction provides improvement in the strength and compressibility of the clay (Pakbaz and Alipour, 2012). Lime has also been widely used to improve the properties of clay soils. Lime reacts with water within the clay, and thereby releases calcium cation (Ca\text{2}+) and hydroxyl anions (OH\text{−}) in solution. The calcium-saturated solution surrounding the clay mineral particles result in cation substitution and particle flocculation and agglomeration, thereby modifying the clay. Under conditions of a high pH, slower, and longer-term stabilization reactions occur, resulting in gel formation and subsequent crystallization (Lim et al., 2002).

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

2. Materials and Methods

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

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.

3. Results and Discussion

3.1. Minerological analysis of kaolinite

Kaolinite material used in this study can be classified as CH-Class (LL>50) high plasticity clay according to the Soil Classification System (USCS). To determine the particle size distribution of the kaolinite, tests including sample preparation ASTM D421 (1985), sieve analysis for coarse particles ASTM D422 (1963), and hydrometer tests for fine particles ASTM D422 (1963) were implemented. According to hydrometer test it was determined that kaolinite had high clay content. Clay and silt content of kaolinite was found to be 85% and 15% respectively. High LL value can be attributed to high clay content of the kaolinite
resulting high swelling property. XRD and FT-IR analysis were implemented for CH class kaolinite. XRD analysis gives mineralogical composition of the material. Kaolinite mineralogically contains quartz (SiO₂), kaolinite (Al₂Si₂O₅(OH))₄ and alunite (KA1₃(SO₄)·OH₆). Quartz represents the purity of the material.

BET analysis gives surface area of mesopores, macropores and micropores, volume of macropores and micropores and diameter of macropores and micropores of the kaolinite. Total surface area, macropore surface area and micropore surface area of kaolinite was determined to be 27.315, 22.049 and 5.266 (m²/gr), respectively. Macropores volume and micropores volume were found to be 0.120 and 0.006 cc/gr whereas macropore diameter and micropore diameter were determined to be 19.483 Å and 8.800e+00 Å, respectively. It was found that the kaolinite had a remarkable BET surface area, which was primarily contributed by mesopores and macropores. It can also be concluded that kaolinite has a macroporous 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. In the FT-IR spectrum of kaolinite peak at 691and 1026 cm⁻¹ indicates Si-O structures on the surface of kaolinite. The peak observed at 795 cm⁻¹ can be assigned to Si–O–Si structures associated with pronounced concentration of silicon in the sample corresponds to cellulose on the surface. The peaks at 3691, 3650 and 3620 cm⁻¹ could be assigned to hydroxyl groups probably attributed to adsorbed water. The band centered at 911 cm⁻¹ in the FT-IR spectra of sewage sludge was assigned to Al-O-H structures in the region and the peak observed at 1003 cm⁻¹ indicates Si-H structure.

3.2. Effect of salt solution on Consistency limits of Kaolinite and kaolinite mixtures

Variation in index parameters (Liquid Limit, Plastic Limit and Plasticity Index) of kaolinite and kaolinite mixtures is given in Figure 1-3. It can be seen from Figure 1 that that liquid limit values of of kaolinite and all kaolinite mixtures prepared with cement, gypsum and lime decreased as the NaCl concentration increased. The decrease was more significant at lower concentrations. The plastic limit increased and plasticity index also decreased for salt concentrations between 0.01 and 1 N. Before the soil samples were exposed to salt concentrations, it was observed that gypsum and cement increased liquid limit values of the samples whereas lime decreased.

The thickness of the DDLs is an important controlling factor for the structural development, hydraulic conductivity, and other physico-chemical and mechanical properties of soils (Yılmaz et al., 2008). The thickness of DDLs around clay particles is governed by the concentration of salt and type of cation(s) in the soil water. In CH clay samples; as the concentration of the salt solutions increases, the thickness of DDL decreases resulting in flocculation of the clay particles and larger pore channels through which flow can occur. It can also be concluded that many chemicals tended to reduce the thickness of the DDL, causing the soil skeleton to shrink and causing a decrease in repulsive forces, thus promoting flocculation of clay particles, and dehydration of the interlayer zones of expandable clays, which subsequently became gritty or granular (Bowders and Daniel; 1987). Kaya and Fang (2000) indicated that as repulsive forces decreased, the soil particles tended to flocculate and form aggregates due to attractive forces among particles, leading to a net increase in the
effective flow area, resulting in increased hydraulic conductivity of the soil-pore fluid (Yılmaz et al., 2008).

Results of the study is found to be consistent with the several researchers who have reported that chemical solutions at low concentrations are more effective than at high concentrations for CH clays (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 (Schmitz et al., 2004; Arasan and Yetimoglu, 2008). Furthermore, most other researchers have indicated that the hydraulic conductivity increased when the concentration of inorganic salt solutions increased as similar to the findings of the present study (Jo et al. 2005; Kolstad et al. 2004; Lee and Shackelford 2005; Yılmaz et al., 2008).

It can be seen from Figures 1-3 that additive materials provide improvement in engineering properties of kaolinite. The decrease in Liquid Limit values and increase in Plastic Limit values are determined to be lower as additive materials were used. In this study salt solutions simulate leachate and the effect of leachate on consistency limits thereby hydraulic conductivity was investigated. It was observed that additive materials avoid significant change in consistency limits. As decrease in Liquid Limit values of liner materials can be limited, increase in hydraulic conductivity will also be limited.

Figure 1 Effect of NaCl solutions with different concentrations on Liquid Limit values of kaolinite and kaolinite mixtures

![Graph showing the effect of NaCl solutions on Liquid Limit values of kaolinite and kaolinite mixtures](image-url)
4. Conclusion

This study was undertaken to investigate the effect salt solutions (NaCl) simulating leachate on consistency limits of liner materials (CH class kaolinite and kaolinite mixtures). Results of the study showed that liquid limit and plasticity index values decreased as the concentration of salt solutions increased for all liner samples while plastic limit values increased. The variations in consistency limits were found to be higher at low concentrations.
of salt solutions. Decrease in liquid limit values of the of the mixtures prepared by addition of cement, lime and gypsum was found to be lower as compared with that of kaolinite solely. 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 can migrate from leachate to groundwater more easily. It should also be pointed out that further studies on the geotechnical properties of CH class clays (such as stress–strain, compressibility, swelling, and consistency limits) permeated with chemicals are needed to make more reasonable judgments concerning their use for waste disposal landfill design.

References


Determination of Transport Coefficients of Inorganic Contaminants Through Alternative Liner Systems from Leachate to Groundwater Using One-Dimensional Mass Transport Model

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Keywords: 1-D mass transport model, Inorganic contaminant transport, Heavy metals, Inorganic macrocomponents, Leachate, Liner systems

Abstract

In the present study one-dimensional (1D) advection–dispersion transport modeling was conducted for evaluation of inorganic (heavy metals and inorganic macrocomponents) contaminant transport through alternative liner systems from leachate to groundwater. Ten identical pilot-scale landfill reactors with different alternative composite liners were operated for a period of about 290 days and transport coefficients of heavy metals and inorganic macrocomponents were determined. Results of the study showed that Pb had the highest dispersion coefficient ($48.77 \times 10^{-8}$ m$^2$/s) whereas Ni had the lowest dispersion coefficient ($2.07 \times 10^{-8}$ m$^2$/s) among all heavy metals and K had the lowest dispersion coefficient ($1.5 \times 10^{-8}$ m$^2$/s) among inorganic macrocomponents. The results obviously indicated that the transport of inorganic compounds to the groundwater can be noticeably decreased with the particular use of bentonite and lime materials in composite liner systems. Utilization of lime prevented heavy metal transport by increasing pH values, thus increasing adsorption capacity of the liners and increasing precipitation ratio of the heavy metals.

1. Introduction

Municipal solid waste (MSW) landfills pose an environmental threat to groundwater resources due to leachate migration. Leachate is highly contaminated and complex structured wastewater consisting of a wide range of toxic inorganic and organic compounds. Pollutants in MSW landfill leachate can be divided into four groups: dissolved organic matter that can be measured as chemical oxygen demand (COD), biochemical oxygen demand (BOD); inorganic macro components; heavy metals; and xenobiotic organic compounds (Kjeldsen et al., 2002). The major sources of heavy metals in landfills are the co-disposed industrial wastes, incinerator ashes, mine wastes and household hazardous substances such as batteries, paints, dyes, inks, etc. (Christensen et al., 2001; Kjeldsen and Christophersen, 2001). Soils have been contaminated with heavy metals such as lead, copper, zinc, iron, manganese, chromium, and cadmium leading to serious problems because heavy metals are unbiodegradable contaminants.

Liner system is one of the most important elements of a modern engineered landfill (Baun et al., 2004). The effectiveness of modern landfill liner systems to minimize migration of organic and inorganic contaminants is of great concern. Composite liners consisting of a geomembrane (usually high density polyethylene (HDPE) 1–2.5 mm-thick) overlying a compacted soil liner (0.30–1.5 m-thick) are the standard design for liner systems in...
municipal solid waste landfills (Slack et al., 2005). Alternative liners are permitted, provided that they are shown to be equivalent to the standard composite liner and in some cases these liners are more effective at preventing groundwater contamination. Popular alternatives are to replace compacted soil liner with a low-cost natural materials or to utilize some materials to decrease hydraulic conductivity of the liner material and avoid contaminant transport. More recently, alternative liner materials have been proposed as a replacement for all or part of the clay component of composite liners, although little field evidence exists regarding their effectiveness at limiting contaminant migration.

The predominant pathways for solute transport through composite liners depend on the type of contaminant; (1) inorganic and organic solute transport through defects in the geomembrane and subsequently through the soil liner by advection and dispersion, (2) transport of organic solutes through the intact geomembrane and subsequently through the soil liner by diffusion (contaminant migration driven by the difference in concentration between the upper and lower sides of the liner) (Boopathy, 1997; Slack et al., 2005; Oman and Junestedt, 2008; Bejerg et al., 2009). Since geomembranes are essentially impervious to diffusion of inorganic solutes (Boyd et al., 1983) and liquid flow (Edil, 2003; Slack et al., 2005; Foose, 2010), the predominant pathway for transport of inorganic solutes is through defects in the geomembrane. Then the solute is transported through the soil liner and underlying soil layers via advection, diffusion, or a combination thereof (Bejerg et al., 2009).

Flow and solute transport through composite liners are three-dimensional processes. The approach used herein is to analyze a one-dimensional system that approximates the characteristics of the three-dimensional system. In this paper, an analytical solution of 1D contaminant transport through alternative composite liner systems was presented under conditions of steady-state flow and transport parameters (dispersion coefficients) of inorganic contaminants were determined. The performance of different liner systems were evaluated by the systematic and comprehensive approach.

2. Materials and Methods

2.1. Reactor setup and operation

Ten pilot-scale landfill reactors (R1-R10) were operated for about 290 days to investigate advective transport of heavy metals representing inorganic contaminants. All parts of the reactors were made of HDPE pressurized pipes with a wall thickness of 0.005 m. The diameter ($D_R$) and height ($H_R$) of the reactors were 0.40 m and 0.80 m, respectively. The diameter and the height of the reactors made of HDPE pressurized pipes were 40 cm and 80 cm, respectively. The reactors were comprised from two parts; consisting leachate in the upper part and distilled water simulating groundwater in the lower part. The bottom of the both parts of the reactors consisted of perforated pipes inserted to collect samples from leachate and groundwater.
Ten alternatives with different composite liners were employed for the reactor liners. The clay material and geomembrane used in this study were obtained from Odayeri Sanitary Landfill in Istanbul, Turkey. Liner systems were constructed at the top of the lower part and groundwater was separated from the liner system by screen-like plastic material. A detailed schematic of the experimental set-up is depicted in Figure 1. The thicknesses of the liners were 20 cm. The total area of geomembrane defects was about 1.0% of the surface area of the reactor. Liner systems of the reactors are given in Table 1. An equivalent hydraulic conductivity \( k_e \) values for the underlying liners consisting of different materials with different hydraulic conductivity values were determined for each reactor system by using the arithmetic average method proposed by Golan and Whitson (1986):

\[
k_e = \frac{k_1 L_1 + k_2 L_2 + \ldots + k_n L_n}{L_1 + L_2 + \ldots + L_n}
\]

Table 1. Liner systems of the pilote-scale reactors and hydraulic conductivity values (m/s)

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Liner</th>
<th>( k_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>%100 Clay</td>
<td>6.3x10^-8</td>
</tr>
<tr>
<td>R2</td>
<td>%100 Bentonite</td>
<td>2.7x10^-10</td>
</tr>
<tr>
<td>R3</td>
<td>%100 Kaolinite</td>
<td>3.2x10^-7</td>
</tr>
<tr>
<td>R4</td>
<td>%100 Zeolite</td>
<td>8.8x10^-8</td>
</tr>
<tr>
<td>R5</td>
<td>%50 Clay + %50 Bentonite</td>
<td>3.16x10^-8</td>
</tr>
</tbody>
</table>
Equivalent hydraulic conductivity ($k_e$) values for the liners of reactors are given in Table 1. The reactors were filled with approximately 36 L leachate and 36 L of distilled water.

### 2.2. One-dimensional mass transport model

In this study, the following assumptions are made for the estimation of transport parameters of the selected inorganic (heavy metals) through an attenuation layer overlying an aquifer with horizontal flow [5]: (1) porous medium is isotropic and saturated, (2) composite liner and underlying geologic layers are horizontal and homogeneous, (3) solute transport in the underlying aquifer occurs only via advection, (3) flow in the aquifer occurs in one-dimensional motion to the layers and is uniform and steady-state, (4) solute transport in the underlying aquifer occurs only via advection, and Darcy’s law is valid, (5) no contaminant decay occurs in the composite liner and underlying geologic layers or aquifer.

In the 1D system (e.g. the $x$ direction), transport by advection–dispersion and hydrodynamic dispersion ($D_x$) can be expressed as follows (Ogata and Banks, 1961):

\[
\text{Transport by advection} = \bar{v}_x n C dA
\]

\[
\text{Hydrodynamic dispersion} = D_x = \alpha_x \bar{v}_x + D_m
\]

where $\bar{v}_x$ is the average linear velocity [L/T], $n$ is the porosity (constant for unit of volume), $C$ is the concentration of solute [M/L$^3$], $dA$ is the elemental cross-sectional area of the conceptual cubic control volume [L$^2$], $D_x$ is the hydrodynamic dispersion coefficient [L$^2$/T], $\alpha_x$ is the longitudinal dispersivity [L], and $D_m$ is the molecular diffusion coefficient [L$^2$/T].

Katsumi et al. (2001) [7] have reported that advective and dispersive transport must be considered for clay liners due to their low hydraulic conductivity. Considering the simultaneous effect of advective and dispersive transport, the diffusive flux ($F_x$) in a 1D system is computed using the following equation (Ogata and Banks, 1961):

\[
F_x = \bar{v}_x n C - n D_x \left( \frac{\partial C}{\partial x} \right)
\]

In the analytical solution of 3D system, total amount of solute entering the conceptual cubic element and the difference in amount entering and leaving the element are expressed, respectively, as follows (Ogata and Banks, 1961):

\[
F_x dy dz + F_y dx dz + F_z dx dy
\]

\[
\left( \frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z} \right) dx dy dz
\]
For a non-reactive solute, the difference between flux in and out can be considered to be equal to the amount accumulated within the element. Therefore, based on the predefined equations, the rate of mass change \( \frac{\partial C}{\partial t} \) in the element is computed by using the advection-dispersion equation as follows (Ogata and Banks, 1961):

\[
\frac{\partial C}{\partial t} = D_x \left( \frac{\partial^2 C}{\partial x^2} \right) + D_y \left( \frac{\partial^2 C}{\partial y^2} \right) + D_z \left( \frac{\partial^2 C}{\partial z^2} \right) - \left[ v_x \left( \frac{\partial C}{\partial x} \right) + v_y \left( \frac{\partial C}{\partial y} \right) + v_z \left( \frac{\partial C}{\partial z} \right) \right]
\]  

(7)

Based on the general assumptions, the solution of Eq. (7) for 1D transport system at an elapsed time, \( t \), can be obtained by (Ogata and Banks, 1961; Katsumi et al., 2001):

\[
\frac{C(x = L, t)}{C_0} = \frac{1}{2} \left[ \text{erfc} \left( \frac{1 - T_R}{\sqrt{2} T_R P_L} \right) + \exp(P_L) \text{erfc} \left( \frac{1 + T_R}{\sqrt{2} T_R P_L} \right) \right]
\]

(8)

where \( L \) is thickness of the clay liner and \( x \) is the vertical downward coordinate with origin at the surface of the liner, \( C \) is the concentration of solute at time of \( t \) (herein described as the average concentration in distilled water), and \( C_0 \) is the initial value of \( C \) at time of \( t \) (herein described as the average concentration in leachate). The parameter \( T_R \) is the dimensionless time factor and \( P_L \) is the Peclet number representing the relative magnitudes of advective and dispersive transport. In Eq. (8), \( T_R \) and \( P_L \) are computed as follows (Katsumi et al., 2001):

\[
T_R = \frac{v_{Sx} t}{R L} = \frac{v_{Sx} t}{(1 + \rho_d K_p / n) L}
\]

(9)

\[
P_L = \frac{v_{Sx} L}{D}
\]

(10)

where \( v_{Sx} \) is the seepage velocity (in the \( x \) direction), \( \rho_d \) is the dry density of the clay, \( K_p \) is the clay-solute partition coefficient, and \( D \) is the dispersion coefficient for the solute. The term \((1 + \rho_d K_p / n)\) in Eq. (12) is called the retardation factor, \( R \). When substituting Eqs. (9) and (10) into Eq. (8), the final form of this equation can be obtained as follows:

\[
\frac{C(x = L, t)}{C_0} = \left[ \frac{R L - v_{Sx} t}{R} \right] \text{erfc} \left( \frac{\sqrt{4 D t}}{R} \right) + \exp \left( \frac{v_{Sx} L}{D} \right) \text{erfc} \left( \frac{\sqrt{4 D t} R}{R} \right)
\]

(11)

In the conceptual approach used herein, retardation factor was selected as \( R = 2 \) (for inorganics) which is consistent with the value assumed by Katsumi et al. (2001) [7]. Eq. (11) is simplified for inorganic compounds as follows (Ogata and Banks, 1961):

\[
\frac{C(x = L, t)}{C_0} = \left[ \frac{R L - v_{Sx} t}{R} \right] \text{erfc} \left( \frac{\sqrt{4 D t}}{R} \right)
\]

(12)
As seen in Eq. (12), leakage through the geomembrane defects is the primary transport mechanism of inorganic contaminants through composite liners. Katsumi et al. (2001) have reported that this flow and transport process is three-dimensional (3D), which makes it difficult to simulate. Therefore, the 3D system can be analyzed readily if it is approximated as an equivalent 1D system having a leakage rate \( Q \) through an area \( (Ae) \) (Slack et al., 2005; Bejerg et al., 2009). In this study, the leakage rate of inorganic contaminants is computed for a circular defect in a composite liner using the following equation (\( h_w < 3 \) m, and defect diameter \( a \leq 5 \times 10^{-5} \) m²) (Giroud, 1997; Erickson and Thiel, 2002; Slack et al., 2005):

\[
Q = C_f \left( 1 + 0.1 \left( \frac{h_w}{L} \right)^{0.95} \right) a^{0.1} \left( \frac{h_w}{L} \right)^{0.9} (k)^{0.74} (N) \tag{13}
\]

where \( Q \) is the leakage rate per unit area (m³/m²/s), \( C_f \) is the related to the quality of the intimate contact between the geomembrane and its underlying clay liner, \( h_w \) is the head of liquid on the top of the geomembrane (m), \( L \) is the thickness of the composite liner (m), \( a \) is the area of single defect in geomembrane (m²), \( k \) is the hydraulic conductivity (herein defined as equivalent hydraulic conductivity, \( k_e \)) of the underlying composite liner (m/s), and \( N \) is the number of defects having area \( a \).

Eq. (13) contains the factor \( C_f \) which accounts for the degree of intimate contact between the geomembrane and its underlying clay liner. Empirical studies indicated that \( C_f \) value of about 0.21 represents compacted clay liner installations with good construction quality assurance achieving “good” liner contact rating whereas \( C_f \) value of about 1.15 represents “poor”, hydraulic contact between a geomembrane and a compacted clay liner. Moreover, a conservative value of \( C_f = 0.01 \) was recommended by Thiel et al. (2001) for “excellent” contact conditions. In a specific design, liquid head build-up, \( h_w \), may vary from less than 0.025 m for cap applications, up to 0.30 m for regulated applications. Based on the above-mentioned facts, in this study, we set the depth of leachate (\( h_w \)) 0.03 m. \( C_f \) value value was selected as 0.01 indicating a conservative contact rating. The length of the simulation time was about \( t = 290 \) days and the leakage rate \( (Q) \) was computed in m³/s for a reactor surface area of about \( A_R = 0.126 \) m² (for \( D_R = 0.40 \) m).

**Table 2.** Parametric values used in 1D advection-dispersion model for the estimation of the transport parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Head of liquid on the top of the geomembrane (( h_w ))</td>
<td>0.30 m</td>
</tr>
<tr>
<td>Thickness of the HDPE geomembrane (( L_g ))</td>
<td>0.002 m</td>
</tr>
<tr>
<td>Thickness of the composite liner (( L_e ))</td>
<td>0.20 m</td>
</tr>
<tr>
<td>The quality of the intimate contact between the geomembrane and its underlying clay liner (( C_f ))</td>
<td>0.01</td>
</tr>
<tr>
<td>Retardation factor (( R ))</td>
<td>2.0</td>
</tr>
<tr>
<td>Inorganics</td>
<td></td>
</tr>
<tr>
<td>Frequency of geomembrane defects (( N ))</td>
<td>1</td>
</tr>
<tr>
<td>Area of single defect in geomembrane (( a ))</td>
<td>5x10⁻⁵ m²</td>
</tr>
<tr>
<td>Surface area of the reactor (( A_R ))</td>
<td>0.126 m²</td>
</tr>
</tbody>
</table>
Table 2 summarizes the selected parametric values used in 1D advection-dispersion model for the estimation of the transport parameters. Based on the above-mentioned design considerations and the continuity equation, the seepage velocity ($v_{Sx}$) in transport of inorganic constituents through geomembrane defects in composite liners Eqs. (1) and (13) as a function of thickness of the composite liner ($L$) and the equivalent hydraulic conductivity ($k_e$):

$$v_{Sx} = f(L,k_e) = (0.02134) \left(1 + 0.1 \left(\frac{0.30}{L}\right)^{0.95}\right)(k_e)^{0.74}$$  \hspace{1cm} (14)

When substituting the selected retardation factors and simulation periods ($R = 2$ and $t = 290$ days) into Eqs. (11) and (12), dispersion ($D_d$) coefficients are calculated for inorganic contaminants, as follows:

$$D_m = f(L,C,C_0) = \left(\frac{0.022 L}{\text{erfc}^{-1}\left(\frac{C}{C_0}\right)}\right)^2$$  \hspace{1cm} (15)

$$D_d = f(L,v_{Sx},C,C_0) = \left(\frac{L - (257.09)(v_{Sx})}{32.07 \text{ erfc}^{-1}\left(2C \right)\left(\frac{C}{C_0}\right)}\right)^2$$  \hspace{1cm} (16)

3. Results and Discussion

A simplified one-dimensional (1D) advection-dispersion transport model approximating three-dimensional (3D) processes (flow and solute transport) occurring in landfills was conducted to simulate inorganic contaminant transport through alternative landfill liners and to estimate the transport parameters as similarly conducted by Foose (2010). Schematic presentation of dispersion coefficients of inorganic contaminants are shown in Figure 2.

The results indicated that Pb had the highest dispersion coefficient ($48.77 \times 10^{-10}$ m$^2$/s) among all inorganic contaminants whereas Ni had the lowest dispersion coefficient ($2.07 \times 10^{-10}$ m$^2$/s) among all heavy metals and K had the lowest dispersion coefficient ($1.5 \times 10^{-10}$ m$^2$/s) among inorganic macrocomponents. It is noted that the effect of the various geochemical processes on the transfer of contaminants might be different due to differences in mobility and physio-chemical behavior of each inorganic contaminant, as similarly reported by Ladha (1999). The results obviously indicated that the transport of inorganic compounds to the groundwater can be noticeably decreased with the particular use of bentonite and lime materials in composite liner systems.

As can be seen from Figure 2 dispersion coefficients estimated for the R2, R5, R8, R9 and R10 reactor systems were found to be lower than those obtained for other reactor systems. Low dispersion coefficients of heavy metals determined for R9 (90% clay + 10% lime) and R10 (90% bentonite + 10% lime) reactor systems can be explained by increasing adsorption capacity of the materials due to high pH values obtained by lime. This findings are consistent with the results concluded by Lu et al. (2011). Precipitation processes and physical sorptive mechanisms are dominant in the mobility of metals (Ozel, 2007) and high
precipitation and sorption efficiencies are achieved at high pH values. It can also be seen in Figure 2 that heavy metal transport in R2 (100% bentonite), R5 (50% bentonite+50%clay) and R8 (80% bentonite+20%zeolite) reactor systems were fairly lower. Kjeldsen et al. (2002), Ozel (2007) [20] and Haijjan et al. (2009) concluded that higher CEC values indicates higher negative charge of clay fraction, thicker double layer hence higher heavy metal sorption capacity. CEC values of R2, R5, R8, reactors liner systems were determined to be 48.62 meq/100 g, 39.45 meq/100 g, 50.46 meq/100 g, which are much higher than that of other reactors liner systems (Varank et al., 2017). Since heavy metal migration is inversely proportional with the adsorption capacities of liner materials and adsorption capacities of liner materials are directly proportional with CEC values of the materials. Additionally, contaminant transport occurs slowly in liner systems with low hydraulic conductivities. The hydraulic conductivity values were determined to be 3.1x 10^{-7} for kaolinite, 6.3x 10^{-8} for clay, 8.8 x 10^{-8} for zeolite and 2.7 x 10^{-10} m/sn for bentonite. Since bentonite material had the lowest hydraulic conductivity value and highest CEC value as compared with alternative liner materials, dispersion coefficients of the inorganic contaminants were found to be lower in the liner systems where bentonite was used.

4. Conclusion

In this study, simplified 1D advection–dispersion transport model was performed to evaluate inorganic contaminant transport from leachate to groundwater through composite liners. Although predictions of contaminant transport described herein were limited by the assumptions and some boundary conditions, the simplified 1D transport model can readily be used for the preliminary comparison of the performance of different mineral liner systems. Ten pilot-scale landfill reactors were operated for a period of about 290 days to examine advective transport of heavy metals and inorganic macrocomponents. Results of the study indicated that for all inorganic contaminants, dispersion coefficients estimated for the R2, R5, R8, R9 and R10 reactor systems were found to be lower than those obtained for other reactor systems. Pb had the highest dispersion coefficient (48.77 × 10^{-10} m^2/s) among all inorganic contaminants whereas Ni had the lowest dispersion coefficient (2.07 × 10^{-10} m^2/s) among all heavy metals and K had the lowest dispersion coefficient (1.5 × 10^{-10} m^2/s) among inorganic macrocomponents. Results showed that average dispersion coefficients of inorganic contaminants were lower in the reactors where bentonite and lime materials were used. This can be explained by adsorption and precipitation mechanisms that are dominant in heavy metals mobility. The findings of this study clearly demonstrated utilization of alternative liner materials especially bentonite and lime highly prevented inorganic contaminant transport from leachate to groundwater.
Figure 2. Schematic presentation of dispersion coefficients of heavy metals and inorganic macrocomponents.
References


Treatment of Tannery Industry Wastewater by Electrocoagulation Process Using Iron Electrodes

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Keywords: Tannery industry wastewater, electrocoagulation, iron electrodes, cost

Abstract

This work deals with investigation of electrocoagulation process for tannery industry wastewater treatment. The removal of COD, TSS and color from tannery wastewater was experimentally investigated using iron electrodes. Effects of initial pH, electrolysis time and current were examined. Optimum values of operational parameters were experimentally determined for maximum COD, TSS and color removal. The batch experimental results revealed that COD, TSS and color removal efficiencies were 77, 96 and 96 % under optimum conditions (pH: 8, electrolysis time: 60 min, current: 3 A). Operational cost are calculated as 6.80 €/m³ for optimum conditions. The results of the experimental study showed that the electrocoagulation process using iron electrodes is an effective treatment method for tannery wastewater.

1. Introduction

The tannery industry is one of the industries with high water consumption. The tannery industry wastewater includes high levels of salinity, organic pollution, inorganic matter, dissolved suspended solids, organic nitrogen and specific pollutants (Song et al., 2004). Characterization of tannery industry wastewater considerably changes depending on the size of the industry, the chemical variety and amount used, the amount of water used and the final product (Durai and Rajasimman, 2011).

Various treatment methods such as coagulation-flocculation (Haydar and Aziz, 2009; Mella et al., 2018), biological treatment (El-Sheikh et al., 2011; Balaguér-Arnandis et al., 2017) and advanced treatment processes (Liu et al., 2017; Selvabharathi et al., 2016) are used in the treatment of wastewater of tannery industry. In commonly used chemical treatment methods, the chemicals used bring secondary pollution and intense sludge formation. Conventional biological treatment methods are insufficient in pollutant removal due to the low biodegradability of the tannery industry wastewater.

Electrocoagulation is a common process used for electrochemical treatment. In the electrocoagulation process, suspended, colloidal, or dissolved pollutants in aqueous media can be removed by coagulation, adsorption, absorption, precipitation, and flotation mechanisms (Aygün, 2012). The electrocoagulation process is considered to occur in three consecutive stages:

- Electrolytic oxidation of the electrodes, formation of coagulants,
- Destabilization of pollutants, particle suspension and emulsion breakage,
- Collection of shocks in destabilized phases.
When iron is used as an anode, Fe(OH)\(_n\) (\(n = 2\) or \(3\)) forms iron hydroxides in the electrolytic system. The formation of metal hydroxides is shown as two mechanisms in equations (1-8).

1. Mechanism:

Anode:

\[
\begin{align*}
4Fe(s) & \rightarrow 4Fe^{2+}(aq) + 4e^- \\
4Fe^{2+}(aq) + 10H_2O(l) + O_2(g) & \rightarrow 4Fe(OH)_2(s) + 8H^+ \tag{2}
\end{align*}
\]

Cathode:

\[
8H^+(aq) + 8e^- \rightarrow 4H_2(g) \tag{3}
\]

2. Mechanism:

Anode:

\[
\begin{align*}
Fe(s) & \rightarrow Fe^{2+}(aq) + 2e^- \\
Fe^{2+}(aq) & \rightarrow 2OH^-(aq) \rightarrow Fe(OH)_2(s) \tag{5}
\end{align*}
\]

Cathode:

\[
\begin{align*}
2H_2O(l) + 2e^- & \rightarrow H_2(g) + 2OH^-(aq) \tag{7}
\end{align*}
\]

This paper presents the results of lab-scale studies on COD (chemical oxygen demand), TSS (total suspended solids) and color from tannery industry wastewater treatment by electrocoagulation process using iron electrodes. To optimize the removal efficiency, conditions such as pH, current and operation time were investigated.

2. Materials and Methods

In this study, tannery industry wastewater was used. The wastewater sample was stored at 4 °C and the analyzes were performed according to the Standard Methods recommended (APHA, 2005). The characterization of wastewater is shown in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD, mg/L</td>
<td>3853±251</td>
</tr>
<tr>
<td>NH(_3)-N, mg/L</td>
<td>566,2±37.7</td>
</tr>
<tr>
<td>TKN, mg/L</td>
<td>833,8±40</td>
</tr>
<tr>
<td>TSS, mg/L</td>
<td>1465±60</td>
</tr>
<tr>
<td>TVSS, mg/L</td>
<td>1170±79,5</td>
</tr>
<tr>
<td>Chloride, mg/L</td>
<td>21443,5±277</td>
</tr>
<tr>
<td>pH (20 °C)</td>
<td>3,98±0.05</td>
</tr>
<tr>
<td>Conductivity, mS/cm</td>
<td>43,8± 1.02</td>
</tr>
<tr>
<td>Color, Hazen</td>
<td>700±10.5</td>
</tr>
</tbody>
</table>
The experiments were conducted at ambient temperature (≈20 °C) with 500 mL wastewater gently stirred at 200 rpm in the plexiglass reactor. Different pH (4-9), time (5-80 min) and current (1-5 A) arrangements were studied in order to determine optimum conditions for COD, TSS and color removal from tannery industry wastewater. At the end of each run, the floated and precipitated materials were withdrawn and the clarified effluent sample was pipetted out from the reactor and then allowed to settle for a few hours in a polyethylene flask. Finally, the clarified supernatant liquid was collected and preserved according to the Standard Methods. The COD, TSS and color concentrations of effluent were measured at supernatants. The removal efficiency of each pollutant (R) was calculated using the following equation:

$$R(\%) = \frac{(C_0 - C_t)}{C_0} \times 100$$

where $C_0$ and $C_t$ represent, respectively, the initial and the effluent concentrations of COD, TSS or color.

3. Results and Discussion

3.1 Effect of pH, operation time and current on COD, TSS and color removal

It has been established that the initial pH is an important operating factor influencing the performance of electrocoagulation process (Adhoum & Monser 2004; Chen 2004; Chen et al. 2000; Sekman et al. 2011). Bensadok et al. (2008), determined maximum removal rates at neutral pH 6-7 which is in agreement with many previous works related to EC using aluminum electrodes (Inan et al. 2004; Koby et al. 2003; Sanchez-Calvo et al. 2003).

Figure 1 present the plot of COD removal versus pH for iron electrodes with a contact time of 30 min, at 2 A current. COD removal efficiency was strongly correlated with increase in pH. Rapid removal was noticed initially which declined gradually until reaching equilibrium and remained constant thereafter. It can also be seen from Figure 1 that highest COD removal efficiency (77%) was obtained at pH 8. Thus, optimum pH was determined to be 8.

Figure 2 shows the effect of operation time on COD removal under pH 8 and 2 A conditions. COD removal efficiency increased rapidly up to 60 minutes, then declined. After the experimental studies, the optimum operation time on COD removal was chosen for 60 min.

Experimental studies were carried out under pH 8 and 30 min to determine the effect of current on COD removal. As can be seen from Figure 3, as current increase, COD removal efficiency increased. COD removal increased rapidly up to 3 A, then no significant difference occurred. The optimum current for COD removal was found to be 3 A. Sekman et al. (2011) concluded that the sludge production was increased when current density was increased and correspondingly, the water quantity was decreased. Also it is indicated that the amount of the produced sludge increased with the increasing removal rate of SS, COD, and oil & grease. As applied current density increased, the removal rate of fluoride increased and higher sludge production was observed. The results are consistent with those concluded by Sekman et al. (2011).

The effect of operation time on TSS removal was given in Figure 4. The highest removal was obtained as 96% at 60 min. After 60 min, no significant difference at TSS removal was observed. Therefore, optimum operation time on TSS removal was determined to be 60 min.
Figure 5 shows the effect of operation time on color removal with pH 8 and 3 A. Likewise COD and TSS removal, the highest color removal (96%) was obtained at 45 min.

3.2. Cost evaluation

Operational cost analysis plays an important role in the treatment of industrial wastewaters, as treatment process should be cost effective. The amount of energy consumption, the amount of electrode material EC process for the estimation of operational costs. The operating cost was calculated by the equation as follows:

Operating cost = ENC + ELC

where ENC is energy consumption (kWh/m³), ELC is electrode consumption (kg/m³).

The ENC was calculated using the following equation:

\[
ENC = \frac{U \times i \times t_{EC}}{V}
\]

where U is the applied voltage (V), i is the current intensity (A), tEC is the reaction time (h), and V is the volume of treated wastewater (m³).

The ELC was calculated by the following equation:

\[
ELC = \frac{i \times t_{EC} \times M}{z \times F}
\]

where tEC is the reaction time, M is the molecular mass of the electrode (g/mol), and Z is the number of electrons transferred (zFe = 3), F is the Faraday constant (96, 487 C/mol). The EC process using Fe electrodes was determined to be 6.80 €/m³. It can be concluded that the EC process using iron electrodes can be recommended as effective processes for tannery wastewater treatment.

Figure 1. Effect of pH on COD removal from tannery industry wastewater
Figure 2. Effect of operation time on COD removal from tannery industry wastewater

Figure 3. Effect of current on COD removal from tannery industry wastewater

Figure 4. Effect of operation time on TSS removal from tannery industry wastewater
4. Conclusions

The treatment by electrocoagulation of tannery industry wastewater highly concentrated in COD, TSS and color was investigated using iron electrodes. The optimum conditions were determined to be pH 8, current 3 A and 60 min for COD and TSS removal and 45 min color removal. At optimum conditions 77% COD, 96% TSS and 96% color removal was achieved. The results also showed that the EC process using iron electrodes can be recommended as effective processes for tannery wastewater treatment.

References

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

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

Abstract

Effluents from sewage treatment works are a major source of antibiotic resistance. As such, they create a serious risk to public health and in ecosystems (Ben et al., 2017). Recently, treatment alternatives including ozonation, photochemical treatment processes and catalytic oxidation have been explored and compared to conventional disinfection methods. In the present study, the application of alternative, sustainable and at the same time advanced, high-performance treatment systems including iron-based advanced oxidation processes for the elimination of antibiotic resistant bacteria and their genetic materials was examined. Within the scope of this study, some heterogeneous iron-based catalytic oxidation processes including zero-valent iron (Fe0) and goethite (α-FeOOH)-activated hydrogen peroxide was applied to simulated urban wastewater containing the conjugative, multi-antibiotic resistance plasmid RK4 carrier multi-resistant E-coli J54 strain. Disinfection performance (removal of antibiotic resistance) was compared with those of conventional disinfection processes (chlorination, ozonation and UV-C radiation). The inherent advantages of using iron-based advanced oxidation processes in eliminating not only antibiotic residues but also antibiotic resistance could be demonstrated.

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

1. Introduction

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

2. Materials and Methods

In the present study, owing to its conjugative multi-antibiotic resistance plasmid RK4, the ampicillin (AmpR), kanamycin (KmR) and tetracycline (TcR) multi-resistant *E. coli* J53 strain and its *bla* TEM-2 (ampicillin resistance gene), *aphA* (kanamycin resistance gene) and *tetA* (tetracycline resistance gene) antibiotic resistant genes located on the RK4 plasmid were selected as models to examine the elimination of antibiotic resistance from simulated urban wastewater (COD=150 mg/L; BOD$_7$=200 mg/L; TOC=50 mg/L) by employing heterogeneous, iron-based advanced oxidation processes (zero-valent iron and goethite-activated hydrogen peroxide). For this purpose, synthetic urban wastewater samples will be prepared and thereafter contaminated with multi-antibiotic resistant *E. coli* J53 cells. Beforehand, the selected advanced treatment processes will be optimized in terms of the operating variables pH (3.5 and 5.5), oxidant (hydrogen peroxide, 0-1.0 mM) and heterogeneous iron catalyst (Fe$_0$-ZVI- and α-FeOOH-FeOOH; recommended dose: 1 g/L) concentrations. Their inactivation performance will be examined by following the number of alive, multi-resistant *E. coli* cells as well as the gene copy numbers of the *bla* TEM-2, *aphA* ve *tetA* -resistant genes before and after application of iron-based advanced oxidation processes. The inactivation performance of the iron-based advanced oxidation processes will be evaluated and compared with conventional disinfection processes (chlorination, ozonation and direct UV-C photolysis).

3. Results

3.1. Conventional disinfection processes

The experimental conditions that were selected for the conventional disinfection methods are summarized in Table 1.

<table>
<thead>
<tr>
<th>Disinfection Type</th>
<th>Chlorination</th>
<th>UV-C Treatment</th>
<th>Ozonation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dosages</strong></td>
<td>0,5,10,25,50,100 and 200 mg/L prepared from a 45000 mg/L stock HOCl solution.</td>
<td>For 2,5,10,15,20,30 min at an incident photon flux range of 748-751 lx</td>
<td>Ozone feed rate: 566.4 mg/h≈9 mg/min</td>
</tr>
<tr>
<td><strong>Volumes (mL)</strong></td>
<td>100</td>
<td>400</td>
<td>200</td>
</tr>
<tr>
<td><strong>pH (-)</strong></td>
<td>5.5-5.7</td>
<td>5.5-5.7</td>
<td>5.5-5.7</td>
</tr>
<tr>
<td><strong>Time (min)</strong></td>
<td>30 min</td>
<td>2-30 min</td>
<td>1-10 min</td>
</tr>
<tr>
<td><strong>Initial TOC (mg/L)</strong></td>
<td>10.46</td>
<td>8.39</td>
<td>6.30</td>
</tr>
</tbody>
</table>

Performance of the preliminary disinfection experiments was comparatively examined by measuring the total organic carbon (TOC) content of the samples and calculating removal efficiencies. The initial and final TOC values of the simulated urban wastewater during conventional disinfection was determined as follows;
• For chlorination with HOCl in the range of 10.46-10.37 mg/L
• For UV-C treatment in the range of 8.39-8.25 mg/L
• For ozonation in the range of 6.30-4.56 mg/L (before and after 10 min ozonation)

Considering the initial and final TOC values being measured during the conventional disinfection experiments, a considerable TOC removal was found only after ozonation of the simulated wastewater at high ozone doses (for 10 min at 9 mg/min). Under these circumstances, 28% TOC removal was obtained. This is not surprising due to the fact that TOC removals are only expected under harsh treatment conditions and in the presence of strong and relatively less selective oxidants such as ozone.

In the light of the obtained findings (TOC removal rates) and previous related scientific literature reports, it was decided to follow the fate of antibiotic resistant E-coli bacteria under the experimental conditions given in Table 2.

Table 2. Experimental conditions that were selected for inspection of the antibiotic resistant E-coli

<table>
<thead>
<tr>
<th>Disinfection type</th>
<th>Dosage</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV-C Treatment</td>
<td>758 lx</td>
<td>5 and 20</td>
</tr>
<tr>
<td>Ozonation</td>
<td>9 mg/dk</td>
<td>1 and 5</td>
</tr>
<tr>
<td>Chlorination*</td>
<td>10 and 100 mg/L*</td>
<td>30</td>
</tr>
</tbody>
</table>

*At the end of this experiment (chlorination) 10% w/w (0.4 M) NaNO3 was added to the reaction solution at a concentration being equivalent to 10 and 100 mg/L HOCl to stop the reaction.

3.2. Disinfection with heterogeneous catalytic oxidation processes

Table 3 presents the experimental conditions that were investigated for the advanced heterogeneous catalytic oxidation processes.

Table 3. Experimental conditions of the heterogeneous catalytic oxidation processes.

<table>
<thead>
<tr>
<th>Disinfection Type</th>
<th>SDD</th>
<th>SDD/HP*</th>
<th>FeOOH</th>
<th>FeOOH/HP*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dosages</td>
<td>ZVI: 1g/L</td>
<td>ZVI: 1g/L 0.2,0.4,0.6,0.8,1.0 mM HP</td>
<td>FeOOH: 1 g/L</td>
<td>FeOOH: 1g/L 0.2,0.4,0.6,0.8,1.0 mM HP</td>
</tr>
<tr>
<td>pH (-)</td>
<td>3.5 and 5.5</td>
<td>3.5 and 5.5</td>
<td>3.5 and 5.5</td>
<td>3.5 and 5.5</td>
</tr>
<tr>
<td>Time (min)</td>
<td>0.5,10,20,40,60,80</td>
<td>0.5,10,20,40,60,80</td>
<td>0.5,10,20,40,60,80</td>
<td>0.5,10,20,40,60,80</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>8.87</td>
<td>7.49-7.96</td>
<td>10.94</td>
<td>10.19-7.80</td>
</tr>
</tbody>
</table>

*The reaction was ceased with 10% w/w (0.4 M) NaNO3 addition corresponding to 1.0 mM HP. In this study, 30% w/w (9.79 M) HP stock solution was used to adjust HP concentrations.

The ZVI, ZVI/HP, FeOOH and FeOOH/HP heterogeneous catalytic oxidation systems were comparatively evaluated on the basis of TOC measurements and TOC removal calculations. TOC results for the heterogeneous catalytic oxidation processes are summarized below;

Results of ZVI and ZVI/HP treatment:

• No TOC removal was obtained for ZVI treatment (8.865-8.201 mg/L TOC range at pH 5.5) in the absence of HP.
• No TOC removal was obtained for ZVI/HP treatment with 0.2 mM HP at pH5.5 (8.542-8.521 mg/L TOC range), however, 32% TOC removal was obtained at pH3.5 at the same HP dose (7.854-5.347 mg/L TOC range).
• No TOC removal was obtained for ZVI/HP treatment with 0.4 mM HP at pH5.5 (7.486-7.538 mg/L TOC range), however, 54% TOC removal occurred at pH3.5 (8.043-3.743 mg/L TOC range).
• 41% TOC removal was observed after ZVI/HP treatment at pH3.5 (7.948-4.666 mg/L TOC range) with 0.6 mM HP.
• 25% TOC removal was obtained after ZVI/HP treatment at pH3.5 (6.053-4.548 mg/L TOC range) with 0.8 mM HP.
• 42% TOC removal was found after ZVI/HP treatment at pH3.5 (7.964-4.607 mg/L TOC range) with 1.0 mM HP.

Results of FeOOH and FeOOH/HP treatment:
• 24% TOC removal was observed for FeOOH treatment without HP addition (10.940-8.311 mg/L TOC range) at pH5.5.
• 29% TOC removal was obtained with FeOOH/HP treatment at pH5.5 with 0.2 mM HP (10.19-7.216 mg/L TOC range).
• 31% TOC removal was obtained with FeOOH/HP treatment at pH5.5 (10.26-7.135 mg/L TOC range), 49% TOC removal was evident at pH3.5 (10.26-5.206 mg/L TOC range) in the presence of 0.4 mM HP.
• 9% TOC removal was observed for FeOOH/HP treatment at pH3.5 (7.803-7.099 mg/L TOC range) in the presence of 0.6 mM HP.
• No TOC removal was achieved for FeOOH/HP treatment at pH3.5 (7.026-7.394 mg/L TOC range) in the presence of 0.8 mM HP.
• 17% TOC removal was obtained for FeOOH/HP treatment at pH3.5 (8.519-6.929 mg/L TOC range) in the presence of 1.0 mM HP.

Considering the above findings, it was decided to inspect the fate of resistant *E. coli* bacteria under the following experimental conditions of advanced heterogeneous catalytic oxidation;

• ZVI/HP treatment process: 1 g/L ZVI; 0.4 mM HP; t:20 min; pH:3.5
• FeOOH/HP treatment process: 1 g/L FeOOH; 0.4 mM HP; t:60 min; pH:3.5

From the above experimental results it is also evident that pH as well as HP concentration both play a critical role in the treatment performance of ZVI/HP and FeOOH/HP advanced heterogeneous oxidation processes. In the forthcoming experimental part of the study, the fate of resistant *E-coli* bacteria will be evaluated.
References


Degradation of the Endocrine Disrupting Micropollutant Bisphenol A with Persulfate - and Peroxymonosulfate-enhanced Ozonation Processes

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Keywords: Endocrine disrupting pollutants, bisphenol A, enhanced ozonation, toxicity, degradation products, experimental design

Abstract

The potential endocrine disrupting micropollutant bisphenol A (BPA) was treated by ozonation and persulfate/peroxymonosulfate-enhanced ozonation. Preliminary baseline experiments indicated that aqueous BPA (2 mg/L; 8.8 μM) degradation could be enhanced by persulfate (0.25 mM) and peroxymonosulfate (0.25 mM)-enhanced ozonation compared to the single ozonation process. Analysis of degradation products (carboxylic acids) and quenching studies employing free radical probe chemicals indicated that the reaction mechanism changed during enhanced ozonation; however, still a hydroxyl radical-dominated oxidation mechanism was most important. Acute toxicity of aqueous BPA solutions decreased after ozonation and enhanced ozonation, but could not be entirely eliminated during advanced oxidative treatment in particular at elevated BPA concentrations. Ozonation and enhanced ozonation processes were modeled and optimized for different initial BPA concentrations by experimental design-response surface methodology and analysis of variance.

1. Introduction

Recently, a vast number of micropollutants originating from domestic, industrial and agricultural activities have received serious attention because they are threatening the environment and public health. A large number of these emerging contaminants are termed “endocrine disruptors” due to their ability to cause serious malfunction of the endocrine system in several organisms. The extensive use of bisphenol A (BPA) in the plastics and epoxy resins industry has led to increasing reports of its presence in the aquatic environment (as high as 15-20 mg/L in landfill leachate) as well as realization of its potential negative health impacts including cancer, obesity, heart diseases and other body malfunctions. Hence, their effective control and elimination is a major task in water and wastewater management. Until now, various advanced treatment methods including advanced oxidation processes have shown to effectively degrade BPA (Chen et al., 2007; Torres et al., 2007; Huang et al., 2009; Huang and Huang, 2009; Rodriguez et al., 2010; Santiago et al., 2011; Postigo et al., 2011; Tay et al., 2012). Due to increasing operational reliability and cost effectiveness, there is a great potential for the real-scale treatment of BPA with ozone and enhanced ozonation systems (Umur et al., 2013). In order to enhance the ozonation process, strong oxidants such as persulfate (PS) and peroxymonosulfate (PMS) are employed. Although the PS/O3 and PMS/O3 oxidation systems have already been studied for micropollutant removal, further investigation is urgently needed for a better understanding of the fate of BPA during ozonation as well as the dominant reaction mechanism and aquatic toxicity of BPA’s ozone degradation products.
2. Materials and Methods

All ozonation and enhanced experiments were conducted in 400 mL-capacity glass washing bottles at a constant ozone feed rate of 7.5 mg/min and the original pH (7.5-8.0) of distilled water. Aqueous BPA solutions were prepared in distilled water at varying initial concentrations (2-10 mg/L). After preliminary baseline experiments (ozonation, 0.25 or 0.50 mM PS or PMS-enhanced ozonation of 2 mg/L aqueous BPA solutions), 28 experiments were carried out as foreseen by the RSM-ANOVA design tool that was used to model and optimize the ozone and PS-enhanced ozonation of BPA. Moreover, within the scope of the present study, evolution of carboxylic acids and changes in acute (*Vibrio fischeri*) toxicity were also followed during ozonation and enhanced ozonation of BPA samples to elucidate the nature as well as ecotoxicological risk of the proposed treatment processes. Residual BPA, PS, PMS and O$_3$ concentrations were all measured as described in previous works or in accordance with Standard Methods (APHA-AWWA-WPCF, 1999).

3. Results

3.1. Preliminary baseline experiments

BPA degradation could be enhanced by ozonation with 0.25 and 0.50 mM PS, whereas PMS (0.25 and 0.50 mM) had no remarkable effect on BPA removal with ozone. BPA removal was complete at an ozone dose of 30 mg in the presence of 0.25 mM PS; however, 60 mg ozone was required for ozonation with 0.25 mM PMS. For mere ozonation (in the absence of oxidants), an excessive ozone dose (> 60 mg) was needed to achieve complete BPA removal. As expected, ozone absorption rates increased upon PS addition (from 55% to 60%) due to enhanced ozone decomposition to free radicals such as HO•, or SO$_4$•-, whereas PMS surprisingly had a slightly “stabilizing effect” on ozone absorption (decreasing from 55% to 50%) rates.

3.2. Evolution of carboxylic acids

Formation of carboxylic acids was also followed during ozonation and enhanced ozonation processes. Malonic, muconic and oxalic acid were detected during O$_3$/PS and O$_3$/PMS treatments of BPA right after 1 min ozonation, which completely depleted after 8 min treatment. During mere ozonation (without oxidants), malonic and oxalic acid formation was delayed but quantified after 2 min ozonation, whereas malonic acid disappeared after 6 min ozonation in the absence of oxidants.

3.3. Experiments with probe chemicals (free radical quenching studies)

In order to elucidate the dominant reaction mechanism of ozonation and enhanced ozonation, two different free radical probe chemicals (ethyl alcohol; EtOH, and tert-butyl alcohol; TBA) were used at excessive concentrations (44 mM; BPA : probe chemical molar ratio = 1:5000) during ozonation and enhanced ozonation experiments. Results indicated that in the presence of EtOH, BPA removal via ozonation was seriously inhibited (dropping from 92% to 70%), whereas no inhibition was observed in the presence of TBA, indicating that hydroxyl radicals may not be the dominant oxidizing agent. In the case of PS-enhanced ozonation, both alcohols inhibited BPA removals (from 100% to 83% with EtOH and 85% with TBA), whereas in the presence of PMS, the addition of the alcohols did not appreciably retard BPA removals (only by 10% for EtOH; i.e. from 100% to 90%). From the results it could be inferred that the reaction mechanism is rather complex and differed according to the type of ozonation process.
Particularly hydroxyl radicals were involved in PS-enhanced ozonation of BPA (Figure 1) which may not be expected during mere ozonation at neutral pH conditions.

Figure 1. Degradation of aqueous BPA with ozone (O₃), persulfate (PS) and peroxymonosulfate (PMS)-enhanced ozonation processes (PS/O₃; PMS/O₃) in the absence and presence of the hydroxyl radical (HO●) probe chemical tert-butyl alcohol (TBA). Reaction conditions: 2 mg/L BPA; 0.25 mM PS or PMS; 44 mM TBA; applied ozone dose 7.5 mg/min; initial pH 6.5.

3.4. Experimental design and validation experiments (in terms of treatment performance and changes in *V. fischeri* toxicity)

The target of the validation experiments was decided to be “highest BPA removal” at the “original pH of the reaction solution” and “minimized treatment time (ozone dose)” and/or “PS concentration”. These targets were set at five initial BPA concentrations (2, 4, 6, 8 and 10 mg/L).

The validation experiments foreseen by RSM-ANOVA are given in Table 1, whereas Table 2 presents experimental and model results of the validation experiments.

Table 1. Conditions of the validation experiments carried out according to the experimental design tool. Ozonation and PS-enhanced ozonation processes were selected for the experimental design of BPA treatment.

<table>
<thead>
<tr>
<th>Validation Experiment Nr.</th>
<th>Initial BPA Concentration (mg/L)</th>
<th>Initial PS Concentration (mg/L)</th>
<th>Initial pH (-)</th>
<th>Ozonation Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>0</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>0.5</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>0.5</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>0.5</td>
<td>8</td>
<td>6.5</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>0.5</td>
<td>8</td>
<td>6.5</td>
</tr>
</tbody>
</table>
Table 2. Experimental and foreseen model results of the validation experiments. Experimental conditions are as in Table 1 for ozonation and PS-enhanced ozonation of aqueous BPA solutions

<table>
<thead>
<tr>
<th>Validation Experiment Nr.</th>
<th>BPA removal (experimental, %)</th>
<th>BPA removal (model, %)</th>
<th>O₃ Consumption (%)</th>
<th>PS Consumption (%)</th>
<th>Percent Relative Inhibition (initial-final, %)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>95.5</td>
<td>100</td>
<td>92</td>
<td>0</td>
<td>22-3</td>
</tr>
<tr>
<td>2</td>
<td>87</td>
<td>91</td>
<td>94</td>
<td>16</td>
<td>35-10</td>
</tr>
<tr>
<td>3</td>
<td>81</td>
<td>87</td>
<td>94</td>
<td>22</td>
<td>45-12</td>
</tr>
<tr>
<td>4</td>
<td>95</td>
<td>90</td>
<td>96</td>
<td>26</td>
<td>53-21</td>
</tr>
<tr>
<td>5</td>
<td>90</td>
<td>100</td>
<td>95</td>
<td>26</td>
<td>58-32</td>
</tr>
</tbody>
</table>

*after 15-min incubation with *V. fischeri* photobacteria

Separate bioassays were also conducted to examine the acute toxicity of BPA and its degradation products during treatment with ozone and PS-enhanced ozonation processes. At an initial concentration of 2 mg/L, the acute toxicity towards the marine photobacteria *V. fischeri* decreased from 22% to practically non-toxic levels (< 5%) after 5 min (ozone dose = 38 mg) ozonation in the absence of PS. For the highest examined BPA concentration (10 mg/L) the inhibitory effect could be reduced from 58% to 12% after 6.5 min (ozone dose = 49 mg) ozonation in the presence of 0.5 mM PS.

References


Sepiolite Supported Co-Ce-B Catalyst for Hydrogen Generation from NaBH₄

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

Abstract

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

1. Introduction

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

Sepiolite is a natural clay mineral with a unit cell formula Siₑ₂O₃₀Mg₈(OH)₄(H₂O)₄₈H₂O. The structure of sepiolite formed by tunnels that grow up in the fiber directions and alternative blocks. Each structural block is composed of two tetrahedral silica sheets and central octahedral sheet containing magnesium. Due to the discontinuity of the external silica sheet a significant number of silanol (Si-OH) groups are present at the surface of this mineral [Nunez et al., 2014]. Sepiolite has powerful sorbent abilities so widely used as an adsorbent for different molecules, organic cations and metals.

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

2. Materials and Methods

All chemicals were analytical grade. The sepiolite sample was obtained from Eskisehir and was used as a catalyst support. It was crushed, ground and sieved through a 200 mesh sieve. Sepiolite supported Co-Ce-B catalyst was prepared by impregnation and reduction method, where Co and Ce with the ratio of 1:1 and total metal content 15wt % (Co-Ce / Sepiolite with total metal) was selected. The mole ratio of NaBH$_4$ and the total metal atoms was set 3:1 to ensure complete a reduction reaction.

Catalyst testing with sodium borohydride hydrolysis reaction was carried out jacketed-heated in batch reactor. The volume of hydrogen released during the experiment was measured by a water displacement method. Every time when the hydrogen generation process finished, the catalyst was separated from the solution, washed thoroughly using deionized water, and subsequently reused.

3. Results

**Effect of catalyst amount**

The effect of the catalyst amount on the hydrogen generation rate was studied using three different catalyst amounts (30, 40 and 50 mg) at NaBH$_4$ concentration of 0.7 M and a reaction temperature of 50 °C. As the amount of the catalyst increased, the volume of the generated hydrogen not changed, and the reaction time was decreased from 32 minute to 17 minute (Figure 1). Possibly, the more BH$_4^-$ ions are adsorbed with increasing of catalyst amount, leading to a better interaction between the sodium borohydride and the catalyst [Wang et al. 2017].

![Figure 1](image.png)

**Figure 1.** Hydrogen generation volume as a function of reaction time with Co-Ce-B/Sepiolite catalyst measured at different amount of catalyst by hydrolysis of alkaline NaBH$_4$ solution.

**Effect of NaBH$_4$ concentration**

The effect of the NaBH$_4$ concentration on the hydrogen generation rate was examined using three different NaBH$_4$ concentrations (0.41 M, 0.55 M and 0.70 M) at a catalyst amount of 50 mg and a reaction temperature of 50 °C. When the NaBH$_4$ concentration was increased from 0.41 M to 0.70 M, the generated hydrogen volume was increased from 800 mL to 1350
mL, and also the reaction time was increased from 12 minute to 17 minute (Figure 2). The hydrogen generation rate increased from 8344 mL/min.gCe-Co to 10588 mL/min.gCe-Co with increasing of NaBH4 concentration.

![Figure 2](image)

**Figure 2.** Hydrogen generation volume as a function of reaction time with Co-Ce-B/Sepiolite catalyst measured at different NaBH4 concentration.

**Effect of NaOH concentration**

The effect of the NaOH concentration on the hydrogen generation rate was studied using three different NaOH concentration (0.66, 0.8 and 1.35 M) at NaBH4 concentration of 0.7 M and a reaction temperature of 50 °C. It can be seen from Figure 3 that the hydrogen generation rate firstly increased a little from 10588 mL/min.gCe-Co to 10693 mL/min.gCe-Co with the rising NaOH concentration from 0.66M to 0.8M. when the NaOH concentration increased 1.35M, the hydrogen generation volume decreased from 1350 ml to 1330 ml and the reaction time increased 16.83 minute to 22.58 minute so hydrogen generation rate drop from 10693 mL/min.gCe-Co to 7852 mL/min.gCe-Co.

The findings in this study about NaOH concentration on hydrogen generation rate were similar which reported by Chang et al., (2014). Solution viscosity increased with the NaOH concentration and the increased of viscosity limited the transfer of BH4⁻ ions from the solution to the surface of active sites in catalyst and thus reduced the hydrogen generation rate.
Effect of reaction temperature

Hydrogen generation kinetic was measured at a solution temperature at 30, 40 and 50 °C (Figure 4). As expected, the hydrogen generation rate increases with temperature. When the reaction temperature increased from 30 °C to 50 °C, the hydrogen generation rate increased sharply from 1999 mL/min.gCe-Co to 10588 mL/min.gCe-Co.

Multi-cycle tests

The cycle test of catalyst was investigated to determine the durability of catalyst. It is seen that Figure 5 the reaction finished within 17 minute in the first cycle while it ended within 33.22 minute in the forth cycle. The volume of generated hydrogen was same in the first and second cycle but then it decreases from 1350 mL to 1300 mL in the third and 1210 in the fourth cycle. Hydrogen generation rate decreases from 10588 mL/min.gCe-Co to 10485
mL/min gCe-Co in the second cycle. Therefore, it could be concluded that Co-Ce-B/Sepiolite catalyst is suitable for hydrogen generation from NaBH₄ solution in multicycle.

![Hydrogen generation volume of NaBH₄ as a function of reaction time with Co-Ce-B/Sepiolite catalyst in the multi-cycle tests.](image)

Figure 5. Hydrogen generation volume of NaBH₄ as a function of reaction time with Co-Ce-B/Sepiolite catalyst in the multi-cycle tests.

In this study, sepiolite supported Co-Ce-B catalyst with the %15 wt. metal content was used in the hydrolysis reaction of alkaline NaBH₄ solution to generate hydrogen. The catalytic activity of catalyst was investigated different amount of catalyst, NaBH₄ concentration, NaOH concentration and temperature. Catalyst showed the best catalytic activity in the 50 mg catalyst, 0.70M NaBH₄, 0.66M NaOH concentration and 50 °C. In addition, the value of activation energy for the hydrogen generation process was calculated to be 66.76 kJ/mol. High durability has shown in first and second cycle in the hydrolysis reaction but then catalytic activity decreased for hydrogen generation rate.

References


Optimization of Dilute Acid Hydrolysis of Kitchen Wastes for Bioethanol Production

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Keywords: Acid Hydrolysis, Municipal Solid Waste, Renewable Energy, Biomass, Kitchen Waste

Abstract

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

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

As a result; acid hydrolysis of KWs with H₂SO₄, showed that the amount of soluble sugars obtained could be increased up to the levels of total sugars. Additionaly, we were observed of steam pretreatment which was combination with acid hydrolysis, has positive affect on the formation of soluble sugars.

1. Introduction

The progressive use of biofuels all areas of life (e.g. transportation and production) strongly affects climate change, depletion of fossil fuels reserves and diminishing dependence on imported fuels. This situation leads to international, national and regional level to focus on alternative energy sources for bioethanol production (Vavouraki et al., 2013). Ethanol is a renewable energy resource that is used as a partial gasoline replacement. It is also environmentally-friendly alternative to the gasoline additive methyl tertiary butyl ether (MTBE) and also demand for ethanol will increase with the reduction of crude oil resource.
On the other hand; the increase of ethanol production from corn and similar energetic foodstuffs compete against the corn-based food and feed production (Sun and Cheng, 2005) and its prices. For this reason, we need to find alternative sources of cheap, eco-friendly and renewable raw materials that are not used in the food industry for ethanol production. The use of municipal kitchen wastes for ethanol production not only makes use of these kitchen solid wastes, but also reduces ethanol production cost due to the waste material. Several studies have been reported on the production of lactic acid from food wastes, with periodic or continuous monitoring of pH, but limited studies have reported on bioethanol production from food waste. Kitchen waste (KW) residues are composed of carbohydrate polymers such as starch, cellulose and hemicellulose, lignin, other organic materials (proteins, lipids, acids, etc.) and a remaining, smaller organic part (ash). Hydrolysis of KW may improve the rate of subsequent enzymatic hydrolysis and increase the yields of fermentable sugars from starchy materials (Vavouraki et al., 2013). The dilute sulfuric acid pretreatment can effectively solubilize hemicellulose into monomeric sugars (arabinose, galactose, glucose, mannose and xylose) and soluble oligomers, thus improving cellulose conversion. Compared to other pretreatment methods, it is especially useful for the conversion of xylan in hemicellulose to xylose that can be further fermented to ethanol by many microorganisms (Sun and Cheng, 2005). Kitchen wastes are alternative energy resource for industrial bioethanol production and that hasn't yet been used industrially in Turkey. The use of KWs in the industrial bioethanol production process should be considered as a new approach to the processes of storing and destroying wastes for municipalities as well as being used as a renewable and low cost raw material for the production of fermentable sugars. This paper is a report of the study carried out on saccharification of KWs as a feedstock for bioethanol fermentation. Dilute acid hydrolysis experiments are carried out on using starchy material sample of kitchen waste obtained from the students cafeteria of Köseköy Vocational School of University of Kocaeli (Turkey) were performed for the purpose of determination of the best dilute acid conditions. At the same time, the effect of steam pre-treatment before and after acid hydrolysis on the glucose which is a fermentable sugar was also investigated. This study aims at identifying the most efficient dilute acid concentration in enhancing the production of fermentable sugar for the bioethanol production.

2. Materials and Methods

The effects of reaction and incubation time and dilute acid concentration on hydrolyses were investigated. The method described by Sun and Cheng (2005) was modified and used for dilute acid hydrolysis. KW samples, (1/10 solid/liquid ratio), was soaked in sulfuric acid, (H₂SO₄), at different dilute acid concentrations of 0-5 %, for varying time periods (0-90 min). Additionally, KWs (1/10 solid/liquid ratio), was pretreated in an autoclave at 121°C with residence times of 30, 60 and 90 min after and before pretreated with dilute sulfuric acid. After pretreatment at increasing time and temperature, both raw and treated kitchen waste were analyzed. The yield of the total reducing sugar concentration was assayed by the DNS (dinitrosalicylic acid) method (Miller, 1959). The maximized parameter in this study was set to be the amount of soluble sugars. Three replicates were done for each experiment. The physicochemical analysis of kitchen waste included determination of pH, total solid (TS) and total volatile solid (TVS), moisture and ash, total carbohydrate. The analyses were based on the Standard Method (APHA, 1995). Moisture and ash were determined based on the Standard Method (AACC 44-15.02 and AACC 08-01.01). The remaining percentage was assumed to be the total carbohydrate content (Uncu and
Çekmecelioğlu, 2011). The total carbohydrate amount was determined according to Dubois et al. (1956). Total reducing sugars were determined by the DNS (dinitrosalicylic acid) method using glucose as the standard (Miller, 1959). The sugar composition of the hydrolyzed kitchen waste which was pretreated with best saccharification method obtained from this study, was analyzed by thin-layer chromatography (TLC) using butanol/acetic acid/water (60:20:20 by volume) as solvent according to Kasavi et al., (2012).

3. Results

Prior to chemical pretreatment of kitchen waste (KW), a detailed physicochemical characterization was performed (Table 1).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value(^a), %, (w/w)</th>
<th>Parameter</th>
<th>Value(^a), %, (w/w)</th>
<th>Parameter</th>
<th>Value(^a), %, (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total solids, (TS)</td>
<td>35.02</td>
<td>Moisture</td>
<td>58.18</td>
<td>Total Sugar(^b)</td>
<td>67.20</td>
</tr>
<tr>
<td>Total volatile solids(^c), (TVS)</td>
<td>97.00</td>
<td>pH</td>
<td>6.5</td>
<td>Soluble Sugar(^c)</td>
<td>32.35</td>
</tr>
</tbody>
</table>

\(^a\) Results belong to three replicates  
\(^b\) Composition of food wastes per gram of dry mass. Percentage of total and soluble sugars corresponds to equivalent g glucose per 100 g dry mass of kitchen waste  
\(^c\) Percentage of total and soluble sugars corresponds to equivalent g glucose per 100 g dry mass of kitchen waste

The main characteristic of the sample was its high content of carbohydrates because the places where the kitchen wastes are taken from cafeterias. Comparable compositional analysis has been reported by Vavouraki et al. (2014) and Thembehurkar and Mhaisalkar (2007). Chemical pretreatment of the substrate aimed at increasing the content of soluble sugars of the sample in order to facilitate its subsequent biochemical conversion into ethanol. Figure 1 represents the sugars released after treatment with increasing concentrations of sulfuric acid at various incubation times. Maximum total sugar (282,966 w/w,%) was released during treatment with 5% sulfuric acid at 90 min and 90°C.

![Figure 1. Effect of increasing concentrations of H\textsubscript{2}SO\textsubscript{4} on release of total sugars from kitchen waste.](image)

The effects of hydrolysis period, and acid concentration on acid hydrolysis were investigated by sugar concentration in hydrolysate. The results obtained for the effects of hydrolysis period and, acid concentrations on saccharification of KW are shown in figure 2. There was an increase in reducing sugar with increasing acid concentration for 60 min hydrolysis period. The sugar yield increased up to 3% acid concentration and leveled off at 4 and 5% acid concentrations. The highest sugar yield of 15.96 g glucose/ g dry sample was obtained for 4% acid concentration for 60 min hydrolysis period at 30°C. For 60 min hydrolysis at 60°C the sugar yield increased from 1 to 2% acid concentration. After 2% acid concentration, reducing sugar yield leveled off from 2 to 5% acid concentration (19.77 g glucose/g dry sample). The highest sugar yield for 60 min hydrolysis period at 60°C was...
20.22 glucose/g dry sample g for 2% acid concentration. The sugar yield increased with increasing acid concentration at 90°C, after 2% acid concentration, reducing sugar yield leveled off from 2 to 5% acid concentration (23.08 g glucose/g dry sample), similar to a 60°C (Fig. 2).

![Figure 2. Variation of sugar yield from kitchen waste after H2SO4 hydrolyses at increasing temperature](image)

The maximum value of glucose yield was 23.08 g glucose/g dry sample at 2% sulfuric acid which is lower than that obtained by Jamaludin et. al., (2012) (39.43 g/l from kitchen waste) and Campo et al., (2006) (33.66 g/L, from feed stock materials). Additionally; detailed results of the obtained soluble sugars as a glucose recovery, (%), from H2SO4 pretreatments at 30, 60, 90 min time intervals and 30, 60 and 90°C temperature values are presented in figure 3. The effect of sulfuric acid concentration on glucose recovery (%) from kitchen waste which was pretreatment with increasing sulfuric acid solution is shown in figure 3. There was little difference in glucose yield for sulfuric acid concentrations between 2% and 5% at 30, 60 and 90 min time intervals. For all sample concentrations, reducing sugar yield slightly increased at all temperature and incubation periods. Same results are reported by Ceylan and Ünal, (2015) and Sun and Cheng, (2005). They are also reported an increase in sugar yield with increasing acid concentration (up to 2%).

![Figure 3. Glucose recovery, (%), obtained from kitchen waste after H2SO4 pretreatment at increasing acid concentrations and time intervals at elevated temperatures](image)

4. Conclusions

Biomass pretreatment mainly involves lignocellulosic feedstock hydrolysis with diluted acids to obtain fermentable sugars for further bioethanol production. To this end, sulfuric acid pretreatment numbers of studies have examined the sulfuric acid hydrolysis pretreatment of food wastes and starch-rich feedstocks. This study investigated the influence of acid pretreatment by sulfuric acid of kitchen waste on fermentable sugar production. Acid hydrolysis of KWs with H2SO4 showed that amount of soluble sugars obtained could be increased up to the levels of total sugars. In fact, optimized results proved that chemical pretreatment of KW with sulfuric acid solution at increasing concentration with steam treatment, increased soluble sugar concentration by 96% compared to untreated KW. Chemical pretreatment of KW that comprises most of the fermentable fraction of municipal
solid wastes for the production of degradable carbohydrates seems to provide a promising solution for valorization of these wastes via bioethanol production.

References
Shale gas extraction by hydraulic fracturing and flowback water treatment technologies: A review

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

Abstract

Shale gas is a natural gas considered as a new source of energy worldwide and shale gas extraction began in the 2000s through the use of horizontal drilling and hydraulic fraction methods leading to a decrease in the price of natural gas and oil globally. Hydraulic fracturing and shale gas production lead to several environmental problems and social concerns including atmospheric pollution, freshwater consumption and water pollution, traffic and noise pollution. Hydraulic fracturing requires large amounts of fresh water and suspended sand, called proppants and chemicals. Millions of liters of water is needed during the hydraulic fraction phase of extraction, which is a very important topic from the point of water management in an environment where water scarcity may be faced in the near future due to climate change. This paper reviews the shale gas extraction and production via horizontal drilling and hydraulic fraction methods, flowback water characteristics, treatment methods and even reuse possibilities of flowback water produced from shale gas extraction in order to minimize their environmental risks.

1. Introduction

The three main types of fossil fuels of the global total primary energy supply are natural gas (21.3%), oil (31.5%) and coal (28.8%). Natural gas is used for transportation; heating and electricity generation; it is considered as a resourceful environmentally friendly fuel which plays the most key role in the global energy market (Pacala, 2004; Melikoglu, 2013). Shale gas is, therefore, an unconventional natural gas. Shale formation is a rock having distinguish geological characteristics such as a high impermeability which trap natural gas in shale reservoirs and inhibit any migration (Figure 1) (Kuuskraa, 2004; Golding et al., 2013; Wang et al., 2014a; Melikoglu, 2014). These formations are the result of the sediment accumulation and their pressurized compaction creating a thin layer of shale rock. Shale formation are thus considered as fine-grained sedimentary rocks highly rich with organic material. The anaerobic degradation of the organic deposits and materials within a shale formation leads to the formation of the shale gas.
A study done by the energy information agency (EIA) reports the shale gas and shale oil resources in 41 individual countries taking into consideration that exploration in these countries is still underway and not finish yet. It was found that China occupy about 31.6 trillion cubic meter (tcm) representing the highest recoverable shale gas resource in the world, Argentina come in the second place with (22.7), Algeria (20.0), U.S. (18.8), Canada (16.2), Mexico (15.4), Australia (12.4), South Africa (11.0), Russia (8.1) and Brazil (6.9) noting that all other countries including: South America, Poland, UK, Spain, Eastern/Western Europe, Morocco, Tunisia, Libya, Egypt, South Africa, Mongolia, Thailand, Indonesia, India, Pakistan, Jordan and Turkey exhibit 43.5 tcm (Melikoglu, 2014). Turkey contains two main shale gas basins: Thrace Basin in the European part of Turkey and Anatolia Basin in the Southeastern part of Turkey. Other basin are still under exploration especially in the Black Sea and the Mediterranean regions of the country (Aydemir, 2011). Experts suggests that Turkey may have an enormous 20 tcm of total reserves, but this number is only a prediction since exploration works is not yet completed (Coskun and Ergin, 2013).

1.1. Shale gas extraction

The detonation of atomic bombs in shale gas formation in Nagasaki 1945 leads to the liberation of natural gas where shale gas were first extracted. Extracted shale gas was highly rich in radioactive elements and Rulison. Extraction technologies have been improved with time to become less dangerous (Jenner and Lamadrid, 2013). Nowadays, large volumes of shale gas is usually extracted by the combination of the horizontal drilling and hydraulic fracturing technologies (Shaffer et al., 2013; Wilkinson et al., 2014). The horizontal drilling seems to be better than the vertical one because it ensures a maximum penetration in the rock features followed by a maximum extraction of the available volume of shale gas. Usually, a seismic survey scans is used in order to identify shale gas reservoirs to be drilled, because it gives images of the highly productive zones (Kargbo et al., 2010).

The horizontal drilling technology costs are higher, when compared to the vertical, but it still is more efficient as it can meets the capacity of several vertical wells (Kargbo et al., 2010; Vidic et al., 2013). For this reason, it is more logical and feasible to prefer the horizontal drilling over the vertical one. The extraction process continues with the hydraulic fracturing which is the next step following the drilling. It consists of applying a very high pressure exceeding the tectonic force and rocks tensile by injecting a high volume of water (usually about 10-50 m³/well) in the horizontal well leading to crack and cause the rock at different places to form holes/fissures (Figure 2). Different fracturing materials, such as
proppants, are added to the hydraulic fracturing fluid in order to keep fractures open for a long time making in turn gas release easier (Kargbo et al., 2010). Inhibitors, pH adjustment agents, surfactants, corrosion inhibitors and biocides may be added to the fracturing fluid too (Colborn et al., 2011; Engle et al., 2014; Barbot et al., 2015; Estrada and Bhamidimarri, 2016).

The hydraulic fracturing process use high volumes of hydraulic fracturing fluid which consist of water 3 to 4 millions of gallons usually mixed with different fracturing materials (Kerr, 2010). These materials such as quartz and ceramic are added in low quantity (about 1%). The main role of the fracturing materials is to keep fractures open for a long time even after it is applied. On the other hand, the application of biocides may reduce H2S production associated with the bacterial multiplication preventing in turn the contamination of extracted natural gas and other chemical additives (Kargbo et al., 2010; Kyle et al., 2013). About 10 to 80 % of used hydraulic fracturing fluid returns to the surface. Returning fluid is considered as wastewater that needs to be treated before being discharged or reused (Kyle et al., 2013).

Large volumes of water used in shale gas extraction, mixed with toxic chemicals and additives, is associated with some undesired environmental risks affecting water and air quality threatening in turn. In addition, shale rock fracturing process may result in greenhouse gases emission known by their negative effects on the environment and the climate change (Bădileanu et al., 2015). Shale gas exploration is in certain cases accompanied with low intensive earthquakes. These earthquakes in most cases however do not affect human life. Environmental risks depend on the location, geology of the place and the duration of the exploitation process are the main factors affecting the environmental risks of shale gases extraction. Based on this, a specific environmental assessment and regulation is needed for each shale gas reservoir zone (Wang et al., 2014b).

2. Wastewater from shale gas extraction

Three types of wastewaters results from shale gas extraction: Drilling muds, flowback and produced brine. Drilling muds wastewater is produced in low quantity relative to other. The wastewater is rich in clay and highly dense, because it is used during the drilling phase to lubricate and cool the drill. The second kind of shale gas wastewater is the flowback wastewater which is the part of wastewater that returns quickly to the surface directly after
well drilling. Flowback wastewaters contain high concentrations of metals, organic compounds, hydrocarbons and radionuclides resulting in turn in a high TDS concentration. Produced brine is the third kind of wastewater which stays in contact with shale formation for a long period of time and return to the surface only after the well is started to produce (Figure 2). Produced brine is called as the wastewater with high concentrations of chemicals and additives having extremely high TDS, more than 100.000 mg/L (Melikoglu, 2014).

Flowback water is characterized by a high salinity TDS generally changing between 5000 to 250000 mg/L with an average value of 100000 mg/L. TDS value usually depends on the geological conditions and the salinity level of the underground shale formations (Rahm et al., 2012). Flowback has salinity 6 times higher than the salinity of the sea, while the concentration of the total suspended solids (TSS) change between 0 and 3000 mg/L and the concentration of the oil and grease content vary between 5 and 1000 mg/L. Flowback water contains two main ions that change in a different pattern up to the well age. Chloride (3000-200000 mg/L) rise in concentration with the well age, however sodium (2000-100000 mg/L) is replaced by calcium and magnesium in the long term time (Gregory et al., 2011; Olsson et al., 2013; Engle et al., 2014). Flowback water also contains other ions such as potassium, strontium, barium, magnesium and calcium having a concentration ranging between 0 to 750 mg/L, 0 to 5000 mg/L, 0 to 10000 mg/L, 0 to2000 mg/L and 0 to 20000 mg/L respectively (Olsson et al., 2013). Sulfate (0 - 5000 mg/L), carbonate (0 - 1000 mg/L) and bicarbonate ( 100 - 6000 mg/L) are also other compounds present in wastewater. It was reported that a concentration of 56 mg/L of iodide and 420 mg/L of ammonium may sometimes take place in flowback water (Harkness et al., 2015). In a study it was reported that it has a total hardness level varying between 10000 to 55000 mg/L (Gregory et al., 2011). Solids from the underground rocks and some of the proppant returned back to the surface with wastewater leads to a total suspended solids values ranging between 300 and 3000 mg/L (Jiang et al., 2013).

Some chemicals were added to the fracturing fluid at the beginning of the hydraulic drilling process to facilitate the fracturing operation. These chemicals such as methanol, isopropanol, naphtalene and others are then present in the flowback water in a concentration that changes between 10 to 250 µg/L (Estrada and Bhamidimarri, 2016). Due to these chemicals, the values of the total organic compounds (TOC), chemical oxygen demand (COD) and biochemical oxygen demand (BOD₅) in flowback water may reach 500 mg/L, 175 to 21,900 mg/L and 3 to 2070 mg/L, respectively (Hayes, 2009). Iron, generally found in a maximum concentration of 500 mg/L, is considered as the most important metal in flowback. In a concentration unit of µg/L, it is possible to found some heavy metals in flowback. BTEX (Benzene, Toluene, Ethylbenzene and Xylene) may be found in this type of wastewater in a concentration of up to 100 mg/L. Finally since radioactive isotopes are generally found in the underground shale formation, some isotopes such as radium isotopes having high water solubility can pass to wastewater (Estrada and Bhamidimarri, 2016).

2.1. Flowback water treatment and disposal methods

As it was mentioned before flowback water is characterized by its high TDS levels which make their treatment not possible with the conventional wastewater treatment facilities (Rodriguez and Soeder, 2015). Having said that the shale gas extraction is carried out far away from the residential areas most of the time. For these reasons, efficient and environmentally friendly management methods must be evaluated and effective and feasible
treatment methods should be developed in order to prevent their menacing effects on the environment. Discharge to an industrial wastewater treatment plant, disposal or underground injection, beneficial reuse and recycling are some examples of the possible treatment methods (Theodori et al. 2014).

2.2.1 Flowback water reuse

The internal reuse of flowback water is one of the possible management methods. Flowback water is reused in the hydraulic drilling process many times at a defined period of time. This method has several advantages as it reduces fresh water use, the negative environmental impacts and the treatment costs. The internal reuse method is mostly used in the places where fresh water is difficult to be reach and other suitable alternative methods application is impossible (Gregory et al., 2011). However, this wastewater needs to be pre-treated before being reused because of the high TDS content which may leads to some operational problems. Filtration, gravity precipitation or chemical precipitation are some examples of the possible pre-treatment methods (Shaffer et al., 2013).

2.2.2 Underground injection and disposal

Underground injection (UI) is one of the most common disposal methods used for flowback water with high TDS levels. UI must be done in a controlled manner only if geological conditions and regulations allow it, because of the seismic risks accompanied with the underground injection (Estrada and Bhamidimarri, 2016). Mechanical vapor compression (MVC), reverse osmosis, membrane distillation, forward osmosis and biological methods are the advanced treatment technologies used to reduce TDS levels before water reuse or underground injection (Mantell, 2011). High TDS levels in these wastewaters make them inappropriate for irrigation, because it damages plant life (Adams, 2011).

2.2.3 Minimizing the production of flowback by using alternative fluids and additives

Alternative fracturing fluid other than water could be propane gel fracturing fluids, liquid carbon dioxide fracturing fluids, nitrogen gas and foam fracturing fluids. These fluids show benefits regarding flowback water management. Propane and especially carbon dioxide use help more in gas recovery minimizing in turn the TDS level in the flowback water. The amount of water used for fracturing may be reduced by adding different ingredients such as guar gum which increase water thickness leading to a 45% reduction in water usage. Another way is to use a non-toxic fluid from food-industry ingredients (Rodriguez and Soeder, 2015).

2.2.4 Flowback water treatment by the advanced treatment Technologies

2.2.4.1 Evaporation with the Mechanical Vapor Compression (MVC)

The evaporation technique consists of treating water with high TDS level by separating brine from clean water. The evaporation technology is suitable for the treatment of water produced from different operating and design strategies. An optimization of the heat transfer must be done for the evaporation of water with high salt concentration. In the mechanic vapor compression system, brine is heated by the heated vapor inside the tube evaporator. This system work under an efficient and reliable temperature of 70 °C to minimize the energy need (Ahmadun et al., 2009).
2.2.4.2. Reverse Osmosis

Reverse osmosis is known to be used mostly on sea water desalination. However, this technology is not suitable when the TDS concentration is more than 40000 mg/L (Gregory et al., 2011). An improved vibrate osmosis system is used as an alternative for the treatment of water with high TDS content from the conventional and gas production. However, because flowback water has higher TDS this technology is not applicable. This alternative method is suitable for a TDS concentration lower than 30000 mg/L. Generally, the reuse of flowback water after a partial treatment is more economic and environmentally friendly most of time (Mantell, 2011).

2.2.4.3 Membrane Distillation

The desalination of high salinity waters may be done by the membrane distillation which is a new and promising technique. The separation is based on heating the water stream letting the vapor molecules passes through a porous hydrophobic membrane to the other side having a cold or ambient temperature degree. A temperature difference of 10 to 20 °C is sufficient and water does not need to reach the boiling point. This separation is facilitated by the pressure difference as well, noting that this system operates on temperatures lower than the other traditional distillation methods (Alkhudhiri et al., 2012; Minier-Matar et al., 2014). Membrane distillation is not only used for sea water desalination, but it has also an important in the treatment of flowback water. Recent studies showed that rejection of salt was more than 99.7% for TDS in membrane distillation system (Minier-Matar et al., 2014; Macedonio et al., 2014).

2.2.4.4. Forward osmosis

Forward osmosis is the process by which a semi-permeable membrane and a draw solution characterized by a high concentration of pollutants are used. In this process, the treatment of wastewater is based on the osmotic pressure difference between the draw solution and wastewater to be treated (Jenner and Lamadrid, 2013). FO process works under low pressure operation resulting in a longer lifespan membrane less susceptible to fouling. Therefore, FO process does not need pre-treatment and frequent membrane maintenance making it more advantageous over other alternative treatment technologies (Shaffer et al., 2015). FO has a wide range of application including domestic and industrial wastewater treatment, seawater desalination, food and pharmaceutical industry (Cath et al., 2006). FO operated in an osmotic dilution mode is demonstrated to be an efficient technology for shale gas drilling flowback fluids, it may overcome the irreversible fouling of membrane and the high rejection of organic/inorganic molecules (Kerri et al., 2013). Cellulose triacetate membrane is generally used and commercially available for flowback water treatment showing a delayed buildup of fouling (Gang et al., 2015).

2.2.4.5. Advanced chemical treatment

The treatment of flowback water for the removal of organic carbon and other organic components is usually done by ozonation, sorption with active carbon or aerobic degradation. The application of these processes must be applied after a pre-treatment of wastewater with air flotation (Butkovskiy et al., 2018). On the other hand, flowback water can be treated by other methods such as Fenton, electro-Fenton and electrocoagulation (Rodriguez and Sooder, 2015; Erkan et al., 2017; Turan et al., 2017).
2.2.4.6. Biological technologies

The microbial capacitive desalination cells are a recent proposed flowback water treatment method used for the desalination of produced waters. The system combines electrodes, cation exchange membranes and adsorption for the capacitive desalination and the organic pollutants removal by microbial oxidation. This technology is not tested widely yet, however, researchers reported that this method may achieve an energy-positive desalination (Lester et al., 2013; Stoll et al., 2015; Forrestal et al., 2015). On the other hand, the cultivation of commercial marine microalgae in the flowback water was proposed as a way reducing costs and water needs for microalgae cultivation but not as a treatment technology (Racharaks et al., 2015).

3. Results

Shale gas is considered as a renewable energy taking the attention of researchers in the world. However, the main question regarding the extraction procedure still remains: Can shale gas be regarded as a sustainable energy which can meet human needs now, without affecting the life of the future generation. From the point of environmental view, shale gas exploration risks generally differ up to the geological condition of the well, generally it demands a large amount of freshwater with a high risk of possible contamination for groundwater and surface water. In addition, methane known as one of the greenhouse gases leading to the global warming can also be emitted during well exploration with a possible discharge of some toxic and corrosive byproducts such as benzene, toluene, and formaldehyde, and hydrogen sulfide. A second issue is that the shale gas exploration can sometimes be the cause of some intensive earthquakes not felt by humans. As a conclusion, it can be said that for a better use of this natural resource a number of regulations, policies, guidelines and standards are needed to set to minimize the adverse effects.

References


Synthesis of the Iron Nanoparticles by Using *Pinus brutia* Extract and Hydrogen Gas Production During the Synthesis

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

Abstract

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

1. Introduction

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

2. Materials and Methods

2.2. Preparation of Leach Solution from *Pinus brutia*

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

### 2.3. Nanoparticle Synthesis and Hydrogen Gas Production

In the nanoparticle synthesis, the certain amount of NaBH₄ was added to the as-prepared leach solution (20 mL) into the 100 mL-erlenmeyer flask sealed with stopper and connected with the inverted-placed and water-filled volumetric cylinder. This method could be called as biosynthesis due to the usage of a green source that is an accumulator plant. In this system, the iron cations in the leach solution were reduced to INPs with BH₄⁻ ions and simultaneously, hydrogen gas was produced during the nanoparticle biosynthesis reaction. The amount of the generated hydrogen gas was measured by water displacement method shown in Figure 1 [4].

![Figure 1. Schematic display of INPs biosynthesis and H₂(g) production](image)

The biosynthesized nanoparticles were characterized with UV-vis spectrophotometer, XRD, SEM, and EDX.

### 3. Results and Discussions

#### 3.1. Characterization Studies of IONPs

The formation of INPs was firstly determined by visual observation of the color of the solution containing INPs and then the UV-vis spectra of INPs solution (Figure 2. (a)) was recorded against distilled water with 1 mm optical path length quartz cuvette. As seen in Figure 2. (a), the maximum absorption peak for the black colored solution containing INPs was obtained at 300 nm.

The phases of INPs were determined by XRD analysis method. According to XRD pattern (Figure 2. (b)); the synthesized nanoparticles had characteristic peaks belonging to Fe₃O₄ (magnetite), FeOOH (goethite), γ-FeOOH (lepidocrocite), Fe⁰ (zero valent iron) and NaCl phases. Moreover, some unassigned peaks due to the impurities arising from the accumulator plant structure were seen in XRD pattern [5]. XRD results also showed that there were zero valent iron as well as iron oxide/hydroxide structures in the content of the nanoparticle. Accordingly, the predicted mechanisms occurred during and after the biosynthesis were given as follows [6]:

\[
\begin{align*}
\text{Fe}^{2+}(aq) + 2\text{BH}_4^-(aq) + 6\text{H}_2\text{O}(s) &\rightarrow \text{Fe}^0(k) + 2\text{B(OH)}_3(aq) + 7\text{H}_2(g) & (1) \\
\text{Fe}^{3+}(aq) + 3\text{BH}_4^-(aq) + 3\text{H}_2\text{O}(s) &\rightarrow \text{Fe}^0(k) + 3\text{B(OH)}_3(aq) + 10.5\text{H}_2(g) & (2) \\
\text{Fe}^0 + 2\text{H}_2\text{O} &\rightarrow \text{Fe}^{2+} + \text{H}_2 + 2\text{OH}^- & (3) \\
2\text{Fe}^0 + \text{O}_2 + 2\text{H}_2\text{O} &\rightarrow 2\text{Fe}^{2+} + 4\text{OH}^- & (4) \\
6\text{Fe}^{2+} + \text{O}_2 + 6\text{H}_2\text{O} &\rightarrow 2\text{Fe}_3\text{O}_4(k) + 12\text{H}^+ & (5) \\
\text{Fe}^{2+} + 2\text{OH}^- &\rightarrow \text{Fe(OH)}_2 & (6) \\
6\text{Fe(OH)}_2 + \text{O}_2 &\rightarrow 2\text{Fe}_3\text{O}_4(k) + 6\text{H}_2\text{O} & (7) \\
4\text{Fe}^0 + 3\text{O}_2 + 2\text{H}_2\text{O} &\rightarrow 4\gamma\text{-FeOOH} & (8) \\
4\text{FeOOH} + \text{O}_2 + 6\text{H}_2\text{O} &\rightarrow 12\gamma\text{-FeOOH} & (9)
\end{align*}
\]

According to Eqs. (1) and (2); Fe²⁺ or Fe³⁺ ions were reduced to zero valent iron by BH⁴⁻ ions. However, the zero valent iron nanoparticles were oxidized by exposure of water (Eq.
(3)) or air (Eq. (4)) and thus, iron oxide/hydroxide structures occurred. For this reason, it was suggested that the zero valent iron nanoparticles should be kept in pure ethanol until usage [6].

![Figure 2. (a) UV-vis spectrum of INPs, (b) XRD pattern of INPs](image)

In order to investigate morphology of INPs, SEM analysis was performed. From SEM images (Figure 3. (a)-(b)), it was observed that the average particles size of the synthesized particles were 82.19 nm, and also they had porous and nearly spherical structures. However, some aggregations of the nanoparticles were obtained in the SEM images, which is the disadvantage of the biosynthesis method.

The elemental content of INPs was determined with EDX analysis method. As seen in Figure 3. (c), the element of oxygen (O) was much higher than the other elements due to the oxidation of zero valent iron nanoparticles as indicated in the results of XRD analysis. Furthermore, the elements of Ca, Na, Mg, and Cl were arising from the branches and leaves of *P. brutia*.

![Figure 3. (a)-(b) SEM images of INPs at different magnifications, (c) EDX analysis results of INPs](image)

### 3.2. Hydrogen Production

#### 3.2.1. Effect of Temperature:

It was investigated in the range of 30-65 °C; for this purpose, 0.70 g NaBH₄ was added to the 20 mL of leach solutions at different temperatures and natural pH value (∼1.18), and the produced H₂(g) volumes were noted and presented in Figure 4. (a). It was seen that the produced H₂(g) volumes at 30, 45, and 65 °C increased up to 60, 40, and 7. min, respectively, and thereafter they remained nearly constant. It was concluded that the reaction rate increased with increase in temperature. This case could be explained as follows: the kinetic energies and thus the rates of molecules in the leach solution increased with increase in temperature; by this reason, the reaction took place faster at higher temperatures. The cumulative H₂(g) volumes for three temperatures were given in Figure 4. (b). The cumulative H₂(g) volumes at 30, 45, and 65 °C were determined to be 1500±10, 1510±10, and 1520±10 mL, respectively. Consequently, there was not significant temperature effect on the H₂(g) production and also it could be said that the temperature increased only the reaction rate.
3.2.2. Effect of pH: It was investigated in the range of natural (≈1.18)-9.0; for this purpose, 0.70 g NaBH₄ was added to the 20 mL of leach solutions at different pH values and 65 °C, and the produced H₂(g) volumes were noted and presented in Figure 5. (a). It could be seen that the produced H₂(g) volumes for all pH values increased up to 7. min, and thereafter they did not change with time. The cumulative H₂(g) volumes for different pH values were given in Figure 5. (b).

![Figure 4](image1.png)

Figure 4. (a) The change of the produced H₂(g) volumes at different temperatures with time, (b) The cumulative H₂(g) volumes at 30, 45, and 65 °C

The cumulative H₂(g) volumes at natural (≈1.18), 3.0, 6.0, and 9.0 were determined to be 1520±10, 1590±20, 1710±20, and 1790±20 mL, respectively. As pH of leach solution increased, turbidity was observed in the leaching solution, which was thought to be caused by the precipitation of other macromolecules such as Ca, Mg, K except for Fe in the leach solution, with NH₃ used to adjust the pH. Accordingly, the macromolecules that did not precipitate at low pH values prevented the iron ions from reacting with NaBH₄. As the pH increased, it was considered that as a result of the increase in precipitated macromolecules and thus the further release of iron ions to react with NaBH₄, the amount of synthesized INPs, and thus the produced H₂(g) increased.

![Figure 5](image2.png)

Figure 5. (a) The change of the produced H₂(g) volumes at different pH values with time, (b) The cumulative H₂(g) volumes for different pH values

3.2.3. Effect of NaBH₄ Amount: It was investigated in the range of 0.70-2.50 g; for this purpose, different amounts of NaBH₄ were added to the 20 mL of leach solutions at natural pH value and 65 °C, and the produced H₂(g) volumes were noted and presented in Figure 6. (a). It could be seen that the produced H₂(g) volumes for 0.70, 1.40, 2.00, and 2.50 g NaBH₄ increased up to 7, 22, 39, and 60. min respectively, and thereafter any significant change in the produced H₂(g) volume was not observed. The cumulative H₂(g) volumes for different NaBH₄ amounts were given in Figure 6. (b). The cumulative H₂(g) volumes for 0.70, 1.40, 2.00, and 2.50 g NaBH₄ were observed to be 1520±10, 3000±20, 4100±20, and 5400±20 mL, respectively. Accordingly, the produced H₂(g) volume increased with increase of NaBH₄.
amount adding to leach solution. The limiting reactant was NaBH₄ for the four cases and in this case, due to the fact that there was sufficient amount of iron ion to react with NaBH₄ in the reaction medium; as NaBH₄ amount was increased, the amount of synthesized INPs, and thus the produced H₂(g) increased.

3.2.4. Effect of PVP Amount: It was investigated in the range of 0.1–2.0 g; for this purpose, different amounts of PVP were dissolved into the 20 mL of leach solutions at natural pH value and 65 °C, and then 0.70 g NaBH₄ was added to the prepared solutions. After that, the produced H₂(g) volumes were noted and presented in Figure 7. (a). It was shown that in absence of PVP and in presence of 0.1, 0.5, 1.0, and 2.0 g PVP, the reactions reached to the equilibrium in 7.0, 11.38, 13.50, 19, and 4.10, respectively. Consequently, it was obtained that the equilibrium time of the reaction extended with increase in PVP amount up to 1.0 g/L.

The cumulative H₂(g) volumes for different PVP amounts were given in Figure 7. (b). The cumulative H₂(g) volumes in absence of PVP and in presence of 0.1, 0.5, 1.0, and 2.0 g PVP were found to be 1520±10, 1820±20, 1890±20, 1990±20, and 1350±20 mL, respectively. Accordingly, the cumulative H₂(g) volume increased with increase in PVP amount up to 1.0 g; however, it decreased in presence of 2.0 g PVP. The effect of PVP amount on H₂(g) production could be explained with the molecular structure of PVP.

PVP is a typical homogeneous amphiphilic polymer that has a strongly hydrophilic part (amide group) and a hydrophobic part (alkyl group). For this reason, it has been frequently used as stabilizer agent in the literature. However, some researchers demonstrated that PVP has reductive property for various metals like long-chain alcohols as well as its stabilizer property. The reduction with long-chain alcohols is long-known method for synthesis of metal colloids. Similarly, polymers that have hydroxyl (–OH) end groups could be used as
reductant agent in the synthesis of metallic nanoparticles. Such a polymer could act like a long-chain alcohol and reduce metal ions to metallic nanoparticles. In the literature, PVP has been used in the chemical synthesis of many types of nanoparticles because the commercial PVP has (–OH) end group and this case provides to PVP a reductive property [7, 8]. Therefore, in this study; it was thought that the reason of the increase of the cumulative $H_2(g)$ volume with increase in PVP amount up to 1.0 g depended on the reductive property of PVP. In this case, in the reaction medium; there was also PVP as a reductant agent as well as NaBH$_4$, and thus; since the amount of reductant agent increased in the reaction medium, the amount of synthesized INPs, and thus the produced $H_2(g)$ increased. Moreover, it has been reported in the literature that the reducing reaction with PVP is slower than the case with the other reductant agents [9]. Therefore, it could said that the extension of equilibrium time with increase in PVP amount up to 1.0 g depended on this case. On the other hand, it was considered that the decrease in the produced $H_2(g)$ in presence of 2.0 g PVP depended on the stabilizer property of PVP. Theoretically, during the nanoparticles synthesis, PVP prevents the agglomeration by enclosing the metal ions by means of its hydrophilic and hydrophobic ends. In this study; when there was 2.0 g of PVP, it was thought that PVP prevented the reducing of iron ions with NaBH$_4$ by much higher enclosing the iron ions, and thus it decreased the amount of the produced $H_2(g)$.

According to the obtained results; the optimum conditions for $H_2(g)$ production was determined to be temperature 65 °C, pH=9.0, 2.50 g NaBH$_4$, and 1.0 g PVP. Under these conditions, the maximum $H_2(g)$ volume of 6000±50 mL was achieved in 80 min. The studies about $H_2(g)$ production in the literature were presented in Table 1. Accordingly, it could be clearly seen that the produced $H_2(g)$ volume was much higher than the other studies. Furthermore, with the literature research; it was observed that $H_2(g)$ has been frequently produced by catalytic hydrolysis of NaBH$_4$; however, it has not been found any study about evaluating the production of $H_2(g)$ during the nanoparticle synthesis.

**Table 1.** The studies about $H_2(g)$ production in the literature

<table>
<thead>
<tr>
<th>Material</th>
<th>NaBH$_4$ (M)</th>
<th>Produced $H_2(g)$ (mL)</th>
<th>Reaction time (min)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron nanoparticles</td>
<td>0.925</td>
<td>6000</td>
<td>80</td>
<td>This work</td>
</tr>
<tr>
<td>Modified multi-wall carbon nanotubes</td>
<td>0.50</td>
<td>1000</td>
<td>15</td>
<td>[10]</td>
</tr>
<tr>
<td>Nickel-boride–silica nanocomposite</td>
<td>0.15</td>
<td>650</td>
<td>120</td>
<td>[11]</td>
</tr>
<tr>
<td>Magnetic cobalt/carbon composite</td>
<td>0.125</td>
<td>500</td>
<td>30</td>
<td>[12]</td>
</tr>
<tr>
<td>Poly (2-acrylamido-2-methyl-1-propansulfonic acid)/Ru–Fe nanoparticles composite hydrogel</td>
<td>0.05</td>
<td>246</td>
<td>9.5</td>
<td>[13]</td>
</tr>
<tr>
<td>Poly (Enteromorpha-g-acrylic acid)/Cu nanoparticles composite hydrogel</td>
<td>0.03</td>
<td>240</td>
<td>250</td>
<td>[14]</td>
</tr>
</tbody>
</table>

**4. Conclusion**

It was concluded that by using leach solution, which was prepared from an accumulator plant (a green source), and NaBH$_4$; it is possible to synthesize INPs which can be widely used in many fields such as wastewater treatment, catalyst applications, antibacterial applications, sensor applications, and also simultaneously to produce hydrogen gas.

**References**

Photo Fenton-like Degradation of Methylene Blue with Cobalt Ferrite Nanoparticles

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Keywords: cobalt ferrite nanoparticles, Fenton-like, heterogeneous catalyst, methylene blue, photo degradation

Abstract

In this work, the synthesis and characterization of cobalt ferrite nanoparticles (CoFe₂O₄ NPs) were carried out. The characterization studies confirmed that the synthesized particles were determined to be CoFe₂O₄ NPs in nanoscale and cubic spinel structure. The photo Fenton-like degradation ability of CoFe₂O₄ NPs was also evaluated and the results demonstrated that the synergistic effect of combining of Co and Fe₂O₄ enabled CoFe₂O₄ NPs become the promising photo Fenton-like catalyst for degradation of MB from aqueous solutions. At the optimum experimental conditions (3.0 of initial pH, 25 mM of H₂O₂ concentration, 50 mg/L of initial dye concentration, and 1.0 g/L of catalyst concentration), nearly 100% decolourisation efficiency was achieved after the photo Fenton-like degradation of MB in the presence of CoFe₂O₄ NPs heterogeneous catalyst with near-UV radiation.

1. Introduction

Nowadays, dyes are used in almost all production sectors in industry; therefore dye-laden wastewaters pollute natural waters and lower their value in use. In recent years, advanced oxidation processes (AOPs) such as Fenton and photo-Fenton processes, ozonation, electrochemical oxidation, photolysis with H₂O₂ and O₃ electro-Fenton, which are based on the production and the oxidative action of hydroxyl radicals, have attracted great attention for the treatment of a wide range of organic pollutants in wastewaters. The photo Fenton-like (UV/H₂O₂) process could be used promptly as a hopeful and attractive treatment method for an effective decolorization and degradation of dyes in a textile wastewater. Recently, the using spinel ferrite (MFe₂O₄) magnetic nanocomposites as heterogeneous catalyst especially in wastewater treatment applications, has gained much attention owing to their distinctive magnetic assets and chemical stability. Moreover, it is easy to remove spinel ferrites magnetic nanocomposites from the treated waste by applying external magnetic material and recycled. Cobalt ferrite magnetic nanoparticles (CoFe₂O₄ NPs) are indispensable metal oxide and they have exclusive applications in various fields like sensor, semiconductor photocatalysts, biomedical etc. It is n-type semiconductor, highly stable, small optical band gaps (2.0 eV) making them active under visible light treatment [1]. In the present study, cobalt ferrite magnetic nanoparticles (CoFe₂O₄ NPs) were synthesized, characterized, and used as heterogeneous catalyst to investigate the possibility of decolourisation of Methylene Blue (MB) dye by photo Fenton-like process.

2. Materials and Methods

2.1. The Synthesis of Cobalt Ferrite Nanoparticles

CoFe₂O₄ nanoparticles have been synthesized by chemical precipitation method. The essential mass of ferric nitrate (Fe(NO₃)₃.6H₂O) and cobalt nitrate (Co(NO₃)₂.4H₂O) was
taken in a stoichiometric ratio of 2:1 and dissolved in distilled water. Then, 1M of NaOH aqueous solution was added as a reductant to adjust the pH 10, then the formed solution was kept at an ambient temperature of 80 °C for 3 hours to obtain a thick precipitate. The obtained product was centrifuged using double distilled water and then dried in a hot air oven at 80 °C for 24 h. The dried product was powdered well by a mortar and calcinated at 500 °C for 3 h in a furnace. As a result, CoFe2O4 nanoparticles (CoFe2O4 NPs) were obtained and then the obtained CoFe2O4 NPs were characterized [2].

2.2. Photo Fenton-like Degradation Experiments

Photo Fenton-like activity of CoFe2O4 nanoparticles was examined by evaluating the degradation of organic Methylene blue (MB) dye in the presence of aqueous solution under irradiation of visible light with a high pressure mercury lamp (165 W). In the photo Fenton-like experiments, 0.05 g of CoFe2O4 NPs, except for catalyst concentration experiments, was added to solutions containing 50 mL of MB solution at known initial pH and initial dye concentrations. Prior to irradiating, the flasks containing the solutions were agitated in the water bath in dark for 20 minutes to make certain desorption-adsorption equilibrium of MB aqueous solution with the nanocatalyst. Then the aqueous solution with the catalyst was exposed to light after addition of 5 ml of H2O2 solutions. The samples were taken at predetermined time intervals and they were centrifuged to remove ferrite nanoparticles. The concentration of MB was observed with the UV-vis spectrophotometer at the wavelength of 665 nm. The decolourisation percentage for MB was expressed in terms of the decrease in UV-vis absorbance.

3. Results

3.1. Characterization Studies

Figure 1 showed that CoFe2O4 NPs could be attracted by an external magnet rapidly, which demonstrated that CoFe2O4 NPs had magnetic properties. When the magnet was removed, CoFe2O4 NPs were dispersed readily by shaking.

The morphology of CoFe2O4 NPs was investigated by SEM analysis given in Figure 2. a-h. According to SEM images, it was thought that micromolecule of cobalt surrounded nanoscale iron structures (Fe2O4 NPs). The average diameter of Fe2O4 NPs was determined...
to be 35.75 nm (Figure 1. (d)). Moreover, micromolecule of cobalt disappeared after Fenton-like degradation of MB while the structure of Fe₂O₄ NPs did not change.

Figure 2. SEM images of CoFe₂O₄ NPs at different magnification (a)-(d) before and (e)-(h) after Fenton-like degradation of MB
3.2. Color Removal Studies

The color removal of MB was investigated for various treatment processes. The color removal percentages for different treatment processes of H₂O₂/UV, CoFe₂O₄ NPs/UV, CoFe₂O₄ NPs/H₂O₂, CoFe₂O₄ NPs/H₂O₂/UV, and Fe₂O₄ NPs/H₂O₂/UV were obtained to be 0.85 %, 1.65 %, 4.84 %, 99.99 %, and 2.18 %. It is known that H₂O₂ is decomposed into •OH radicals in Fenton like degradation processes. The color removal studies showed that decomposition of H₂O₂ did not take place under UV light in absence of UV light in this work. Furthermore, CoFe₂O₄ NPs could decompose very little of H₂O₂ in the dark and UV irradiation significantly enhanced H₂O₂ decomposition efficiency. Moreover, CoFe₂O₄ NPs exhibited very poor photocatalytic activity whilst nearly 100 % photo Fenton-like degradation could be achieved by CoFe₂O₄ NPs. However, it was seen that Fe₂O₄ NPs did not have photo Fenton-like catalytic activity, and so; it could be concluded that the addition of cobalt to Fe₂O₄ NPs improve the photo Fenton-like catalytic activity. In these regards, the purposed degradation mechanisms were given as follows [3]:

\[
\begin{align*}
\text{CoFe}_2\text{O}_4 + h\nu \rightarrow &\text{CoFe}_2\text{O}_4 (h^+ + e^-) \quad (1) \\
\text{CoFe}_2\text{O}_4 (e^-) + \text{H}_2\text{O}_2 \rightarrow &\text{CoFe}_2\text{O}_4 + \text{OH}^- + \cdot\text{OH} \quad (2) \\
\text{CoFe}_2\text{O}_4 (h^+) + \text{OH}^- \rightarrow &\text{CoFe}_2\text{O}_4 + \cdot\text{OH} \quad (3) \\
\text{MB} + \cdot\text{OH} \rightarrow &\text{degradation products} \quad (4)
\end{align*}
\]

Accordingly, hole/electron (h⁺/e⁻) pairs were firstly photogenerated on the catalyst under UV irradiation (Eq. (1)). Then, electrons on CoFe₂O₄ NPs were reacted with H₂O₂ to produce both OH⁻ ions and •OH radicals (Eq. (2)). At the same time, photogenerated holes (h⁺) reacted with OH⁻ to yield •OH radicals (Eq. (3)). By this way, the generated •OH radicals attacked to the dye molecules, resulting in the degradation of them (Eq. (4)). The photo Fenton-like degradation of MB by CoFe₂O₄ NPs was also evaluated by recording UV-vis spectra of dye solution by time (Figure 3).

As shown in Figure 3; a maximum absorption peak was observed in the range of 575-675 nm, which was assigned to π-π* transition of –N=N– (azo) bond. The intensity of peak decreased by time depending on the breakage of the –N=N– bond, resulting in the vanishing of the blue color of MB. However, any new peak formation was not observed in the spectra. Furthermore, two bands in the ultraviolet region located at the ranges of 275-300 nm and 250-275 nm were associated with benzene and naphthalene structures in MB, respectively. The intensities of these bands also decreased by time because of aromatic fragmentation in the dye molecule and its intermediates [4].

Figure 3. UV-vis spectra of dye solution by time
The synthesized CoFe$_2$O$_4$ NPs were evaluated as heterogeneous photo Fenton-like catalyst in the degradation of MB because the highest color removal percentage was achieved by this process. The effects of various environmental conditions on the photo Fenton-like reaction were investigated. The obtained results were given as follows.

3.2.1. Effect of Initial pH: The effect of initial pH on the degradation was investigated in the range of 3.0-5.0 and the color removal percentages at the end of 300 min were presented in Figure 4. (a). As shown in Figure 4. (a), 99.49 % color removal could be achieved at the initial pH=3.0 whilst as the initial pH increased from 4.0 to 5.0, the color removal percentage decreased from 29.71 % to 20.11 %. This case could be explained based on the following three factors [5]:

i. The oxidation potential of •OH radicals increases with decrease in initial pH; and thus, the color removal percentages may reduce by increasing in initial pH.

ii. At high initial pH values, H$_2$O$_2$ decomposes to O$_2$ and H$_2$O; and thus lower •OH radicals form during the reaction. As a result of it, color removal percentages may decrease.

iii. More •OH radicals are produced at the strongly acidic medium depending on dissolving of more iron ions; and thus color removal percentages may increase.

Consequently, optimum initial pH was determined to be 3.0.

3.2.2. Effect of H$_2$O$_2$ Concentration: Evaluating of H$_2$O$_2$ concentration is important because the major cost associated with such processes is H$_2$O$_2$ concentration. In this study, the effect of H$_2$O$_2$ concentration was investigated in the range of 25-200 mM and the color removal percentages at the end of 300 min were presented in Figure 4. (b). Accordingly, nearly same color removal percentages (∼99 %) was obtained in the range of 25-100 mM, and it decreased from 99 % to 90 % thereafter. It is well-known that at high H$_2$O$_2$ concentration i.e., beyond 100 mM for this work, scavenging of •OH radicals take place with increase in H$_2$O$_2$ concentration generating perhydroxyl radicals (H$_2$O$_2$ + •OH → H$_2$O + HO$_2$•). Perhydroxyl radical is less strong oxidant as compared to •OH radicals. As a result of this effect, the color removal percentage reduced when H$_2$O$_2$ concentration was increased beyond 100 mM [5]. Therefore, taken into account the process cost; the optimum H$_2$O$_2$ concentration was chosen as 25 mM.

3.2.3. Effect of Catalyst Concentration: The effect of catalyst concentration on the degradation was investigated in the range of 0.25-2.0 g/L and the color removal percentages at the end of 300 min were presented in Figure 4. (c). As shown in Figure 4. (c), catalyst
concentration had insignificant effect on the degradation process. Therefore, taken into account the process cost; the optimum catalyst concentration was obtained as 0.25 g/L.

3.2.4. Effect of Contact Time and Initial Dye Concentration: The effect of contact time on the degradation was investigated for different initial dye concentrations and the obtained results were shown in Figure 5 (a). As can be seen in Figure 5 (a); for all initial dye concentrations, the color removal percentage was increased up to 300. min, and thereafter it remained nearly constant. The effect of initial dye concentration was also evaluated and the color removal percentages at the end of 300 min were given in the bar chart (Figure 5 (b)). Accordingly, the color removal percentage reduced gradually by increasing in initial dye concentration. This case could be ascribed based on the following four factors [6, 7]:

i. As the initial dye concentration increases, the adsorption of dye molecules on the surface of catalyst also increases; and this case prevents the catalyst to absorb the energy. By this reason; lower •OH radicals are generated and thus, the color removal percentages may decrease.

ii. The higher adsorption of dye molecules on the surface of catalyst may block the active sites on the surface of catalyst, causing lower generation of •OH radicals and thus, the color removal percentages may decrease.

iii. When there are more dye molecules in the reaction medium, they compete against the intermediates produced during the reaction and thus, the color removal percentages may decrease.

iv. At the higher initial dye concentration, the photons are blocked before reaching the surface of catalyst, which may cause the decrease in the color removal percentages.

Figure 5. Effect of (a) contact time and (b) initial dye concentration (pH=3.0, 25 mM H2O2, T=25 °C, Xo=0.25 g/L)

4. Conclusions
In this study, the degradation could be achieved in presence of near-UV light when both oxidant (H2O2) and catalyst were present together in the reaction medium, thus proving that the dye was decolorized by photo Fenton-like reaction. According to the obtained results; the optimum initial pH, H2O2 concentration, initial dye concentration, and catalyst concentration for photo Fenton-like degradation of MB with CoFe2O4 NPs were determined to be 3.0, 25 mM, 50 mg/L, and 1.0 g/L, respectively. At these optimum conditions, almost 100% decolourisation efficiency was obtained. Consequently, the present study have revealed significant outputs to synthesis of an effective photo Fenton-like heterogeneous nanocatalyst, which could be important for the contribution to the related literature as well as the water treatment applications.
References


Colorimetric Detection of Fe$^{3+}$ Ions in Aqueous Solution by Using Green-Synthesized Silver Nanoparticles

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Keywords: Bauhinia variegata leaf extract, colorimetric sensor, detection of Fe$^{3+}$ ions, green synthesis, silver nanoparticles

Abstract

In this study, the green synthesis and characterization of silver nanoparticles (AgNPs) from orchid tree (Bauhinia variegata) leaf extract was firstly carried out and then the usability of AgNPs as a colorimetric sensor for detection of Fe$^{3+}$ ions in aqueous solutions was evaluated. The characterization studies showed that the synthesized particles were determined to be AgNPs in nanoscale and face-centered cubic structure. Besides, the total phenolic content of B. variegata extract was determined to be 1.826±2.1 mg gallic acid equivalents/g dry leaf. Also, the green-synthesized AgNPs showed a strong surface plasmon resonance ($\lambda_{SPR}$) around 430 nm and $\lambda_{SPR}$ intensity decreased with the increasing of Fe$^{3+}$ concentration in aqueous solution. Based on the linear relationship between the change of $\lambda_{SPR}$ intensity and Fe$^{3+}$ ion concentration, AgNPs can be used for the sensitive and selective detection of Fe$^{3+}$ ions in aqueous solutions with a linear range of 6-100 μM and a detection limit of 2.08×10$^{-6}$ M.

1. Introduction

There are various analytical techniques such as atomic absorption spectrometry, inductively coupled plasma mass spectrometry, and inductively coupled plasma emission spectrometry for the detection of metal ions. However, these methods usually require sophisticated equipments, technical expertise, and tedious sample preparation steps. Therefore; it is thought that these techniques are not economical and user-friendly. Recently, the colorimetric detection technique has been widely used to detect metal ions in aqueous solutions as it is cost-effective and requires less time. Nowadays, metallic nanoparticles can be widely used for colorimetric detection of metal ions due to their strong surface plasmon resonance (SPR), stable dispersion, bio-compatibility, and controllable physical/chemical properties. Among the metallic nanoparticles; it is well-known that silver nanoparticles (AgNPs) have the strongest SPR; for this reason, most of SPR-related fundamental investigations and sensing applications have focused on AgNPs [1]. For these works, it is important to study with environmentally-friendly and low-cost nanoparticle-based sensor; in this regard, the green synthesis method is frequently preferred for the synthesis of metallic nanoparticles. So; in this study, AgNPs were synthesized with a green, simple, one-pot, low-cost, and stabilizer-free method for the detection of Fe$^{3+}$ ions in aqueous solutions.

2. Materials and Methods

2.1. Green Synthesis and Characterization of AgNPs

Orchid tree (Bauhinia variegata) leaves were collected from Çiftlikköy Campus of Mersin University and then 5 g of the purified and dried leaves were boiled in 600 mL of distilled water. As-prepared aqueous leaf extract was used a reducing agent in the green synthesis of AgNPs. For this purpose, 5.0 mL of the aqueous leaf extract was added to 100 mL of 10$^{-3}$
M AgNO₃ solution. Then, the mixture was stirred magnetically at room temperature for 1 h. After that, the resulting mixture was centrifuged and the precipitated AgNPs were washed with distilled water and dried at 110 °C in an oven for 24 h. Finally 0.015 g of the dried AgNPs were dispersed in 100 mL of distilled water for the colorimetric detection studies. The dried AgNPs were used for characterization studies such as XRD, zetasizer using DLS technique, and FTIR [2].

2.2. Colorimetric Detection

The colorimetric detection studies of the different species such as Na⁺, K⁺, Mg²⁺, Ba²⁺, Ni²⁺, Mn²⁺, Cu²⁺, Zn²⁺, Fe³⁺ and Cd²⁺ with AgNPs were carried out by a series of experiments. 1 ml of 1000 μM metal ion solution was added to the mixture containing 2 mL of 0.15 g/L AgNPs solution and 1 mL of the distilled water. Approximately 5 minutes later, the absorbance value of the prepared solution was recorded at 430 nm by UV-vis spectrophotometer and their spectra were scanned at a wavelength range of 300-700 nm. Experimental and analysis methods were repeated for the other metal ions. The maximum decreasing in the SPR of AgNPs and disappearance of color was observed only in the presence of Fe³⁺. Thus, different concentrations of Fe³⁺ (1-100 μM) were used to determine the linear detectable range and limit of detection by means of decreasing in the λSPR intensity of AgNPs [1].

3. Results and Discussions

The results of the green synthesis, characterization and the colorimetric detection of the metal ions with silver nanoparticles (AgNPs) from orchid tree (Bauhinia variegata) leaf extract were given in the following sub-sections:

3.1. Characterization of AgNPs

The formation of AgNPs was firstly determined by visual observation of the color of AgNO₃-aqueous leaf extract solution and then the UV-vis spectra of the solutions were performed against distilled water with 1 mm optical path length quartz cuvette. Figure 1. (a) showed the UV-vis spectrums of AgNO₃, B. variegata leaf extract, and AgNPs. As seen in Figure 1. (a), the bond at 330 nm was observed for B. variegata leaf extract, which could be attributed to π → π* transitions, being assigned to the presence of polyphenolics as the reductant and stabilizer agent employed for the green synthesis of AgNPs. In the green synthesis method, B. variegata leaf extract was added to AgNO₃ solution, leading to reduction of Ag¹⁺ ions to Ag⁰ (AgNPs) and visual color change from yellow to brown. This color change was due to the excitation of surface plasmon resonance (SPR) of AgNPs. The strong SPR band was noticed around 430 nm. This band was observed in the ideal wavelength range provided for AgNPs solution [3]. Furthermore, the studies in the literature have suggested that the shape of the particles giving SPR peak in the range of 410–500 nm is spherical whilst SPR bands of pentagons and triangular shapes mostly formed in the range of 500-700 nm. This observation suggested that in this study, AgNPs were synthesized in spherical forms [4].

FT-IR analysis was carried out in order to determine the functional groups of AgNPs, and the FT-IR spectrum was presented in Figure 1. (b). Accordingly, the peaks corresponding to O–H group in polyphenolics (3250 cm⁻¹), =C–H alkenes (2983 cm⁻¹), -COOH carbonyl group (1572 cm⁻¹), –C–H alkane (1309 cm⁻¹), C–N stretch aliphatic amines (1100 cm⁻¹), C–N amines (1095 cm⁻¹), C–C bending (660 cm⁻¹) were determined from FT-IR spectra of AgNPs [5, 6]. Furthermore, the total phenolic content of B. variegata extract was determined to be 1.826±2.1 mg gallic acid equivalents/g dry leaf by Folin-Ciocalteu colorimetric method adapted from Slinkard and Singleton (1977). Thus, the obtained FTIR
peaks and the calculated phenolic content confirmed that the phenolic substances in the aqueous leaf extract played important roles in the reduction of Ag\(^{1+}\) (AgNO\(_3\)) into Ag\(^{0}\) (AgNPs).

The crystal phase of AgNPs was determined by XRD analysis method (Figure 2. (a)). The typical powder XRD pattern showed that AgNPs had face-centered cubic structure [7]. However, there were some unassigned peaks indicating the crystallization of bio-organic phase on the surface of the silver nanoparticles due to the leaf extract [8].

![Figure 1. (a) UV-vis spectrums of AgNO\(_3\), B. variegata leaf extract, and AgNPs, (b) FT-IR spectrum of AgNPs](image)

The size distribution analysis of AgNPs was performed by DLS analysis method, and the observed results were shown in Figure 2. (b). Accordingly, the average hydraulic diameter of AgNPs was found to be 22.07 nm with low polydispersity index of 0.238.

![Figure 2. (a) XRD pattern of AgNPs, (b) Size distribution results of AgNPs](image)

### 3.2. Colorimetric detection of metal ions with AgNPs

Firstly, the selectivity of the green-synthesized AgNPs as a colorimetric sensor for various metal ions (Na\(^{+}\), K\(^{+}\), Mg\(^{2+}\), Ba\(^{2+}\), Ni\(^{2+}\), Mn\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\), Fe\(^{3+}\) and Cd\(^{2+}\)) has been evaluated in this study. For this purpose, uniform concentration of various metal salt solutions was separately added to the green-synthesized AgNPs solutions; after that the color changes of the prepared solutions was firstly observed visually and then the absorption spectra were recorded for AgNPs solutions in the absence and presence of various metal ions. The photos and UV-vis spectra of AgNPs solutions as well as the bar chart plotted by using differences between the absorbance of AgNPs solution in the absence and presence of various metal ions were presented in Figure 3. a-c, respectively. It was clearly seen from Figure 3. a and b that AgNPs solution containing only Fe\(^{3+}\) ions had the color change from brown to
colorless and also $\lambda_{\text{SPR}}$ of AgNPs solution containing only Fe$^{3+}$ ions disappeared whilst the colors and $\lambda_{\text{SPR}}$ intensities of AgNPs solutions showed very slight or even no significant changes in presence of Na$^+$, K$^+$, Mg$^{2+}$, Ba$^{2+}$, Ni$^{2+}$, Mn$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, and Cd$^{2+}$ ions. Furthermore, as shown in Figure 3. c, the bar of AgNPs solution in the presence of Fe$^{3+}$ was much higher than the other metal cations, which stated that other metal cations except Fe$^{3+}$ ions had little influence on the green-synthesized AgNPs. The obtained results clearly showed that the green-synthesized AgNPs colorimetric sensor has a good selectivity towards the sensing of Fe$^{3+}$ ions over other cations.

In order to determine the sensitivity of the green-synthesized AgNPs colorimetric sensor for Fe$^{3+}$ sensing, the changes in the AgNPs solution color and $\lambda_{\text{SPR}}$ intensity for different concentrations of Fe$^{3+}$ were evaluated, and the obtained results were presented in Figure 4. a and b. It was evident that as the concentration of Fe$^{3+}$ increased from 1 $\mu$M to 1000 $\mu$M, the color of AgNPs solution altered progressively from brown to colorless (Figure 4. b); and also, $\lambda_{\text{SPR}}$ intensities of AgNPs solutions containing Fe$^{3+}$ ions at different concentrations decreased gradually (Figure 4. a). These results suggested that the green-synthesized AgNPs exhibited Fe$^{3+}$ concentration-dependent colorimetric response.

The limit of detection for Fe$^{3+}$ ions of the green-synthesized AgNPs colorimetric sensor was determined from three times the standard deviation of the blank signal (LOD=3$\sigma$/s). Figure 5 inferred that Fe$^{3+}$ concentration-dependent colorimetric responses of AgNPs were linearly proportional to the concentration of Fe$^{3+}$ ions between 6-100 $\mu$M, and also LOD for Fe$^{3+}$ ions of AgNPs colorimetric sensor was determined to be 2.08×10$^{-6}$ M. In the literature, for the detection of Fe$^{3+}$ ions by AgNPs; Bothra et al. (2013) determined the LOD of p-PDA functionalized AgNPs as 1.29×10$^{-6}$ M [9] and Zhan et al (2012) calculated the LOD of
pyridyl-appended calix[4]arene functionalized AgNPs as $1.25 \times 10^{-4}$ M [10]. The obtained detection limit of the green-synthesized AgNPs colorimetric sensor in this study was found to be relatively better than the reported AgNPs.

The detection mechanism principle of Fe$^{3+}$ ions by the green-synthesized AgNPs is based on the reduction-oxidation reaction. Table 1 exhibited standard reduction potentials for several elements [11]. Theoretically, it is known that the redox reaction that has positive cell-potential ($E^0_{\text{cell}}$ value) occurs spontaneously. For example, according to Eq. (1)-(3); redox reactions of Ag-Cr$^{3+}$ and Ag-Na$^{1+}$ that have negative $E^0_{\text{cell}}$ values do not take place while the spontaneous redox reaction between Ag-Hg$^{2+}$ can take place due to the positive $E^0_{\text{cell}}$ value [12]. However, as seen in Table 1; the potentials of Fe$^{3+}$/Fe$^{2+}$ (+0.77 V) and Fe$^{3+}$/Fe (-0.04 V) are lower than the potential of Ag$^{1+}$/Ag (+0.80 V). Due to the negative $E^0_{\text{cell}}$ values (for $[\text{Fe}^{3+}/\text{Fe}^{2+}]$–Ag $E^0_{\text{cell}}$= 0.77-0.80=–0.03 V; for $[\text{Fe}^{3+}/\text{Fe}]$–Ag $E^0_{\text{cell}}$= -0.04-0.80=–0.84 V), ferric ions do not have enough ability to oxidize elemental silver (AgNPs). This case could be explained with the presence of halide ions (Cl$^-$ ions arising from FeCl$_3$ metal salt solution) in the detection media. The halide ions could strongly coordinate with silver species, resulting in significant decrease of the reduction potential of the silver species. On the other hand; although the halide ions also have similar influences on iron species, it causes much smaller decreasing in the potential of Fe$^{3+}$/Fe$^{2+}$ than the case of silver species. The much higher decreasing of the potential of Ag$^{1+}$/Ag enables the oxidation of elemental silver by ferric ions to become possible by providing positive $E^0_{\text{cell}}$ value. Thus, the redox reaction between AgNPs and Fe$^{3+}$ ions $[\text{Ag} + \text{Fe}^{3+} \rightarrow \text{Ag}^{1+} + \text{Fe}^{2+}]$ occurs [1, 13, 14].

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**Figure 4.** 

a. UV-vis spectra of AgNPs solutions in the absence and presence of Fe$^{3+}$ ions at different concentration  

b. The photos of AgNPs solutions in the absence and presence of Fe$^{3+}$ ions at different concentration
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October 24-26, 2018 - Istanbul / TÜRKİYE

Figure 5. The plot of ΔA values for AgNPs solutions containing Fe$^{3+}$ ions at different concentrations vs Fe$^{3+}$ concentration

Table 1. Standard reduction potentials at 298 K

<table>
<thead>
<tr>
<th>Reduction reaction</th>
<th>$E^\circ$ (V)</th>
<th>Reduction reaction</th>
<th>$E^\circ$ (V)</th>
</tr>
</thead>
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<tr>
<td>Au$^{3+}$ + e$^-$ ⇌ Au</td>
<td>+1.69</td>
<td>Co$^{2+}$ + 2e$^-$ ⇌ Co</td>
<td>-0.28</td>
</tr>
<tr>
<td>Au$^{3+}$ + 3e$^-$ ⇌ Au</td>
<td>+1.40</td>
<td>Fe$^{3+}$ + 2e$^-$ ⇌ Fe</td>
<td>-0.44</td>
</tr>
<tr>
<td>2Hg$^{2+}$ + 2e$^-$ ⇌ Hg</td>
<td>+0.92</td>
<td>Cr$^{3+}$ + 3e$^-$ ⇌ Cr</td>
<td>-0.74</td>
</tr>
<tr>
<td>Hg$^{2+}$ + 2e$^-$ ⇌ Hg</td>
<td>+0.86</td>
<td>Zn$^{2+}$ + 2e$^-$ ⇌ Zn</td>
<td>-0.76</td>
</tr>
<tr>
<td>Ag$^{+}$ + e$^-$ ⇌ Ag</td>
<td>+0.80</td>
<td>Mn$^{2+}$ + 2e$^-$ ⇌ Mn</td>
<td>-1.18</td>
</tr>
<tr>
<td>Hg$^{2+}$ + 2e$^-$ ⇌ 2Hg</td>
<td>+0.79</td>
<td>Al$^{3+}$ + 3e$^-$ ⇌ Al</td>
<td>-1.66</td>
</tr>
<tr>
<td>Fe$^{3+}$ + e$^-$ ⇌ Fe$^{2+}$</td>
<td>+0.77</td>
<td>Ca$^{2+}$ + 2e$^-$ ⇌ Ca</td>
<td>-2.87</td>
</tr>
<tr>
<td>Fe$^{3+}$ + 3e$^-$ ⇌ Fe</td>
<td>-0.04</td>
<td>Na$^{+}$ + e$^-$ ⇌ Na</td>
<td>-2.71</td>
</tr>
</tbody>
</table>

The schematic display of the predicted redox reaction as well as the colorimetric detection of Fe$^{3+}$ ions by the green-synthesized AgNPs was presented in Figure 6. Accordingly; as a result of redox reaction between Fe$^{3+}$ ions and the green-synthesized AgNPs, the color of AgNPs solution decolorized relatively by adding of Fe$^{3+}$ ions at 100 μM while the color vanished by adding of Fe$^{3+}$ ions at 1000 μM.

Figure 6. The illustration of the detection of Fe$^{3+}$ ions by the green-synthesized AgNPs

4. Conclusions

In the present study, AgNPs could be synthesized by using orchid tree (Bauhinia variegata) leaf extract successfully. Then the green-synthesized AgNPs were evaluated as a colorimetric sensor. The limit of detection for Fe$^{3+}$ ions of AgNPs colorimetric sensor was determined to be 2.08×10$^{-6}$ M, which is relatively better compared to the related literature. Consequently, the obtained results showed that the green-synthesized AgNPs can be used as an effective colorimetric sensor for detection of Fe$^{3+}$ ions in aqueous solution. At a later
stage of the study, a number of studies can be performed, such as the functionalization of AgNPs, to improve the LOD value.

References

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

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

Abstract
In this study, silica gel 60 supported iron-zinc bimetallic nanoparticles (Si@Fe-ZnNPs) were synthesized by chemical co-precipitation method. The synthesized Si@Fe-ZnNPs were characterized by SEM, EDX, FTIR, and XRD analysis and they were tested for an adsorbent for removal of Malachite Green (MG) from aqueous solutions. According to characterization results, the cubic structures and nanosized (≈ 30 nm) spherical particles were formed which were dispersed into the surface of silica gel 60. Also, the adsorption bands which were refer to Fe-O stretches and metal-metal stretching vibration of (Zn\(^{2+}\)–O\(^2-\) ) that confirming the formation of Fe-ZnNPs were obtained in the FT-IR spectrum. Si-O-H, Si-O-Si and O-Si-O stretching and bending vibrations also confirmed that silica gel 60 was supported on the Fe-ZnNPs surface. The optimum adsorption conditions were determined as natural pH 3.2 of solution, temperature 50°C, and adsorbent concentration 1.0 g/L. Also a linear increase was observed in equilibrium uptakes of MG when the initial dye concentrations were increased. The experimental equilibrium data was best fitted to Langmuir isotherm model. The maximum monolayer coverage capacity of Si@Fe-ZnNPs for MG adsorption was found to be 666.67 mg/g at optimum temperature. The experimental kinetic adsorption data were defined the best agreement with the pseudo-second order kinetic model. Weber Morris model results showed that both the film (boundary layer) and intra-particle diffusion affected the adsorption process. The thermodynamic studies suggested that the adsorption process was endothermic, non-spontaneous and the positive ΔS value indicated increased disorder at the solid-solution interface during the adsorption.

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

2.1. The synthesis of silica gel 60 supported Fe-Zn bimetallic nanoparticles

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

2.2. Adsorption Studies

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

3. Results

3.1. Characterisation of silica gel 60 supported Fe-Zn bimetallic nanoparticles

The SEM images of the synthesized Si@Fe-ZnNPs at different magnifications are presented in Figure 1 (a,b,c) and (d,e,f) before and after adsorption, respectively.

![Figure 1. SEM images of Si@Fe-ZnNPs a) – 1 µm, 10 KX, b) – 100 nm, 50 KX c) – 100 nm, 100 KX; before adsorption, d) – 1 µm, 10 KX, e) – 100 nm, 50 KX, f) – 100 nm, 100 KX; after adsorption](image)

The SEM images showed that the spherical nanosized (≈30 nm) particles and the cubic structures were formed which were dispersed into the surface of silica gel 60. The signals of Zn element were detected by EDX analysis at regions of the cubic structures. After MG adsorption, as shown from Figure 1 (d,e,f), it was observed that, the morphological structure changed significantly, the spherical nanoparticles were more agglomerated and the structures in the cubic forms were disappeared. The disappearance of the cubic structures
may be indicated that the Zn element (according to EDX analysis) played an important role in the adsorption process.

EDX spectrums before and after adsorption were presented in Figure 2. According to elemental analysis results, the elemental and quantitative weight composition (wt.%) of synthesized Si@Fe-ZnNPs was composed of 6.78% Fe, 44.07 % Zn, 2.44 %Si, 8.56% O and 42.38 % Cl elements. These results revealed that, the signals in the Fe, Zn, O and Si region confirmed the formation of Si@Fe-ZnNPs. After adsorption, the detection of C and N elements in addition to Fe, Zn, Si, O and Cl elements, confirmed the adsorption of the dye molecules onto the Si@Fe-ZnNPs surface.

The XRD pattern of synthesized Si@Fe-ZnNPs was given in Figure 3. The peaks at 2θ = 34° and 45° correspond to ZnO and maghemite (α-Fe₂O₃) structures in the XRD pattern of synthesized Si@Fe-ZnNPs [3] and XRD diagram indicated that, the material was completely amorphous structure due to the change the crystallinity and phase after adsorption (figure not shown).

FT-IR spectrums of Si@Fe-ZnNPs before and after adsorption were presented in Figure 4. As seen from Figure 4, no significant changes were observed in the FT-IR spectrums of Si@Fe-ZnNPs before and after adsorption. Accordingly, the bands at 3650, 1618, and 954 cm⁻¹ corresponded to O-H stretching vibration related to hydrogen bond, strain of $\nu$(C-N) bond and C – O stretching vibration, respectively. Moreover, the adsorption bands at 584 and 467 cm⁻¹ refer to Fe-O stretches of $\alpha$-Fe₂O₃ and metal-metal stretching vibration of (Zn²⁺ – O²⁻ ) in tetrahedral region that confirming the formation of Fe-ZnNPs. Si-O-H, Si-O-Si and O-Si-O stretching and bending vibrations which were observed at1067.8 and 490.96 cm⁻¹ absorption bands, also confirmed that silica gel 60 was supported on the Fe-ZnNPs surface [4,5].
3.2. Effects of Environmental Conditions on the Adsorption

The isoelectric point of Si@Fe-ZnNPs was determined by zeta potential measurement at different pH (2.0 – 7.0) values and the pH change with isoelectric point is presented in Figure 5-a. As seen from Figure 5-a, the isoelectric point of Si@Fe-ZnNPs (pH_{pzc}) was determined as 4.30. It is expected that, the surface of adsorbent was charged negatively at the higher pH values than isoelectric point of adsorbent and adsorption capacity increased due to strong electrostatic attraction between negatively charged adsorbent surface and cationic structure dyestuff. However, no pH adjustment was made in this study since; it was observed that, dyestuff molecules were collapsed when the adsorbent free solutions of MG were adjusted to basic pH values over the isoelectric point of adsorbent. The attitude of the obtaining high adsorption capacity at natural pH as 3.30, can be explained by the natural pH of the solution is near the isoelectric point of Si@Fe-ZnNPs.

The effect of initial dye concentration on adsorption was depicted in Figure 5-b. As can be seen from Figure 5-b, the adsorption capacities increased linearly (q_c=0.9745*C_0, R^2=0.999) in the studied dye concentrations as a result of the increase in the driving force (∆C) to get over mass transfer resistances of the dye between the aqueous and solid phases. Moreover, the obtaining high equilibrium uptakes gives the opportunity to work in the wide dyestuff concentration ranges.

The adsorbent concentration effect on the percentage of adsorption and equilibrium uptake was presented in Figure 5-c. According to Figure 5-c, the equilibrium uptakes of the dye concentrations decreased with increasing the adsorbent concentration from 0.5 g/L to 3 g/L, but; it was seen that the adsorption percentage increased up to 1.0 g/L of adsorbent concentration, and then slightly remained constant with further increase in adsorbent concentration. The decrease in uptake values with increasing adsorbent concentration may be arise from the interaction between adsorbent particles such as aggregation, resulted from high adsorbent concentration. The agglomeration of the adsorbent particles would lead to decrease in active surface area of the adsorbent and an increase in diffusional path length, hence the lower adsorption capacities were observed at high adsorbent concentrations. As a result, the optimum adsorbent concentration was selected as 1.0 g/L for MG dye adsorption onto Si@Fe-ZnNPs.

The effect of temperature was shown in Figure 5-d. According to Figure 5-d, it was seen that high adsorption capacity was obtained with increase in temperature from 25°C to 50°C. Therefore, the optimum temperature value for MG adsorption was determined as 50°C. Based on the results, high operation temperature indicated that, the studied adsorption process was endothermic nature. The temperature effect result 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. The ΔG calculated from equation of \[ΔG = − RT \ln K_c\]; ΔH and ΔS were calculated from the slope and intercept of the Van’t Hoff’s \[\ln K_c=(ΔS/R)−(ΔH/R)1/T\] plot of ln \(K_c\) versus 1/T. In this study, the linear form of Van’t Hoff equation for the adsorption was found as ln \(K_c\) = - 2348.9*1/T + 3.8537 with the regression coefficient 0.999 (data not shown) and the thermodynamic parameters were calculated and were presented in Table 1. According to Table 1, the calculated ΔG values had positive indicating that adsorption was non-spontaneous. The positive value of ΔS suggested that randomness of the adsorbed dye species at the solid–solution interface during adsorption and the studied adsorption system was endothermic (ΔH>0).
Figure 5. Effects of environmental conditions on the adsorption of MG.

Table 1. Thermodynamic parameters

<table>
<thead>
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<th>T(K)</th>
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<td>298</td>
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3.3. Equilibrium, Kinetic, and Mass Transfer Modelling

3.3.1. Equilibrium modelling: The well-known linearized forms of the Langmuir \( [1/qe=1/\theta qb(1/Ce)+1/Qo] \), and Freundlich \( [\ln qe=\ln Kf+(1/n)\ln Ce] \) isotherm models were applied to the experimental equilibrium data for MG adsorption at studied temperatures. The isotherm constants with regression coefficients \( (R^2) \) are presented in Table 2. According to Table 2, Langmuir isotherm model was better agreement with experimental equilibrium data. Also, the experimental and predicted isotherms for adsorption at 50°C was given in Figure 6. As seen from Table 2, Langmuir isotherm model was better agreement with experimental equilibrium data. This result pointed out that, the adsorption occured at specific homogeneous sites within the adsorbent forming monolayer coverage of MG at the surface of Si@Fe-ZnNPs. The maximum monolayer coverage capacity of Si@Fe-ZnNPs was determined as 666.67 mg/g at 50°C which is the optimum temperature. As seen from Table 2, the maximum monolayer coverage capacity values of adsorbent for MG were increased by increasing temperature may be due to the endothermic nature of the studied adsorption process.

3.3.2. Kinetic modelling: The adsorption kinetics were elucidated by correlating the adsorption kinetic data using the linear forms of the Lagergen’s pseudo-first-order \( \log(qe-qt)=\log(qe)-k1t/2.303 \) and the pseudo-second order \([t/qt]=(1/qe^2k2)+(t/qt)\)
For the adsorption of MG onto Si@Fe-ZnNPs, the parameters of the pseudo first-order and pseudo second-order kinetic models with regression coefficients were presented in Table 3. From Table 3, higher values of $R^2$ and the consistency between experimental and calculated uptake values showed excellent fit of the pseudo second order kinetics.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>Langmuir isotherm model $\left[ q_e = \frac{Q_0 b C_e}{1+b C_e} \right]$</th>
<th>Freundlich isotherm model $\left[ q_e = K_F C_e^{1/n} \right]$</th>
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</tbody>
</table>

Consequently, the synthesized Si@Fe-ZnNPs could show well adsorbent property for the removal of hazardous materials from wastewaters.

References


Removal of Reactive Black 5 Dye using Fenton Oxidation from Aqueous Solutions and Optimization of Response Surface Methodology

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Keywords: Color Removal, Fenton Processes, Optimization, Reactive Black 5, Dye

Abstract

In this study, the color removal from anionic Reactive Black 5 (RB5) dye solutions with fenton oxidation was investigated. Central composite design (CCD) in response surface methodology (RSM) was used to optimize the fenton process. pH, dye concentration, Fe\textsuperscript{2+} dose and H\textsubscript{2}O\textsubscript{2} dose were selected as independent variables to RSM and design experiments determined were performed. The experimental parameters and parameter intervals were determined as initial solution pH (2.5-5.5), dye solution concentration (50-350 mg/L), Fe\textsuperscript{2+} dose (25-55 mg/L), H\textsubscript{2}O\textsubscript{2} dose (175-425 mg/L) and constant temperature (30°C).

The color removal performance of the reactants increased with decreasing pH and dye concentration and increasing reactant amounts. The experimental studies showed that the color removal efficiencies of RB5 dye reached over 99%. The conditions giving the maximum removal efficiency for RB5 were obtained as pH: 2.5, dye concentration: 120 ppm, Fe\textsuperscript{2+}: 25 ppm and H\textsubscript{2}O\textsubscript{2} dose: 240 ppm. A full quadratic model equation in which response variable is interacted with independent variables was developed. The model values were in good agreement with experimental values. R\textsuperscript{2} value confirming the reliability of model equation was 96.2%.

1. Introduction

Textile products are used in various fields in our daily life. Because of the differences in the production processes, dyed wastewaters are produced in large quantities and contain different types of pollutants [1]. The dyeing materials are used for textile dyeing since more than 4000 years [2]. The volume of dyestuffs discharged to the receiving water is very high and poses a danger to environment. It affects aesthetically environment, obstructs light and oxygen input to the aquatic atmosphere and causes negative results on the ecosystem [3]. Dyestuffs have synthetic origin and contain complex aromatic structures. Due to the toxicity content, the living things in the receiving environment are adversely affected [4]. Color removal from the wastewaters is difficult due to low biodegradability of the dye materials [5]. For this reason, color removal in wastewater requires the use of mechanical, chemical and advanced treatment techniques instead of conventional treatment methods [6]. Most of studies such as chemical precipitation [7], cheaper natural clays like Montmorillonite [8], illite [9] and clinoptilolite [10], various bio sorbents (fly ash, corn stalk, walnut shells, rice husks, cotton wastes) [11], electrocoagulation [12], photocatalytic oxidation [13], ozonation [14] and Fenton’s oxidation [15,16,17] focused on the color removal. The purpose of oxidation is to convert the chromophoric groups into the colorless state and converts the
reduced intermediates to forms suitable for biological oxidation. Components such as chlorine, chlorine dioxide, hydrogen peroxide, ozone can be used as oxidative reactivity [18].

In this study, color removal was investigated by fenton oxidation which is an advanced treatment technique. The experiments of fenton oxidation were designed by Response Surface Methodology (RSM). RSM uses an experimental design method, a central composite design (CCD), to match a model to the least squares method [19]. The effects of pH, dye concentration, Fe\textsuperscript{+2} dose and H\textsubscript{2}O\textsubscript{2} dose parameters on RB5 decolorization were investigated. A model was developed that gave the change in color removal efficiency depending on the parameters.

2. Materials and Methods

2.1. Experimental

Experimental studies have been carried out on synthetic dye solutions. RB5 dye was selected because of the common use in the textile industry. Fenton oxidation experiments were performed in a one liter volume jacketed reactor. Temperature is controlled with a thermometer and set to 30 °C. 100.000 ppm stock H\textsubscript{2}O\textsubscript{2} and 20.000 ppm stock FeSO\textsubscript{4}.7H\textsubscript{2}O solutions were used at specified doses. First, the pHs of the dye solutions were set to pH values in appropriate range for the fenton process (2<pH<5) using 1 M H\textsubscript{2}SO\textsubscript{4}. Then, fenton oxidation reactant solutions were added in dye solutions and rapid and slow mixing were immediately carried out at 120 rpm for 2 min and 30 rpm for 20 min, respectively. The samples were settled for 30 minutes afterwards. The pH of the supernatant sample was adjusted to 7.5 using 1 M NaOH and left to settle for 1.5 h. [8]. The sample from the upper phase was centrifuged at 5000 rpm for 5 minutes and the color value remaining was measured by the spectrophotometer.

2.2. Analysis

The color of the aqueous dye solutions were measured by colorimetric method. The maximum wavelength of the RB5 was determined of 597 nm. Color removal efficiency was calculated by the following equation;

\[
\text{Color Removal Efficiency, } \% = \frac{[C_0 - C_s]}{C_0} \times 100
\]

*Where, C\textsubscript{0} and C\textsubscript{s} are initial and outward concentrations (ppm).

2.3. Experimental Design

The Central composite design CCD, the most widely used approach of RSM, was employed to optimize the four independent variables which are initial pH, dye concentration, Fe\textsuperscript{+2} doses and H\textsubscript{2}O\textsubscript{2} doses. In the design, 4 factors with 5 different levels, 2 levels of which were out of space, were determined as independent variables and color removal % was response variable. The levels and ranges of independent variables are shown in Table 1.
Abstract Book of the 4th International Conference on Recycling and Reuse
October 24-26, 2018 - Istanbul / TÜRKİYE

Table 1. The levels and ranges of variables in experiment design

<table>
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<tr>
<th>Indipendent Variables</th>
<th>Symbol</th>
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<td>Dye Concentration (mg/L)</td>
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<td>pH</td>
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<td>Fe(^{2+}) doses (mg/L)</td>
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<tr>
<td>H(_2)O(_2) doses (mg/L)</td>
<td>(X_4)</td>
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</table>

3. Results

The experiments were performed at the conditions determined by RSM and experimental and model results are shown in Table 2. Following the experimental design presented in Table 2, an empirical full quadratic model equation, in terms of the four independent variables, as shown in Eq. (2) was developed for color removal (%). The model was confirmed by the high \(R^2\) and fitted well to the experimental data. The correlation coefficients of the model equation were defined as R-Sq = 0,9619 and R-Sq(adj) = 0,9263.

Table 2. RSM experiments along with actual and predicted values of responses

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<th>pH, ppm ((X_2))</th>
<th>Fe(^{2+}) doses, ppm ((X_3))</th>
<th>H(_2)O(_2) doses, ppm ((X_4))</th>
<th>Y, color removal (%)</th>
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</table>
Color Removal RB5 \( (Y) \) = 98,1871 - 0,0487*X1 - 5,2870*X2 - 0,2428*X3 + 0,1570*X4
- 0,0002*X1^2 + 0,2313*X2^2 + 0,0008*X3^2 - 0,0005*X4^4 + 0,0049*X1*X2
- 0,0007*X1*X3 + 0,0005*X1*X4 + 0,0019*X2*X3 + 0,0076*X2*X4 + 0,0011*X3*X4
(2)

3.1. Effect of Fe\(^{12}\) concentration

As seen Figure 1., the color removal performance increases with increasing Fe\(^{12}\) ion concentration in sufficient H\(_2\)O\(_2\) concentration. The removal performance decreases even in the presence of high doses of iron if the sufficient H\(_2\)O\(_2\) is not available in the solution. In case of the sufficient iron ion concentration, Radicals are formed from hydrogen peroxide with high oxidation potential [3].

3.2. Effect of H\(_2\)O\(_2\) concentration

As seen Figure 2., the percentage of decomposition of pollutants generally increases with increasing hydrogen peroxide concentration. It can be explained by increase in the hydroxide radicals with high oxidation potential. The adjustment of the oxidant dose is also important in terms of operating costs [1].
3.3. Effect of pH

It is seen from the Figure 3. that increasing initial pH values effects the removal performance negatively. This is because the reaction rate slows down due to reduction of soluble iron ion types at the high alkaline pH values. If the pH is too alkaline; hydrogen peroxide is catalytically degraded and the activity in the solution decreases [17].

![Figure 3. Effect of initial solution pH to removal efficiency (Constant dye concentration 200 ppm, Fe^{2+} 40 ppm)](image)

3.4. Effect of dye concentration

It can be seen from the Figure 4. that increasing dye concentration reduces the removal efficiency for constant oxidant concentration. The amount of reagent required for the treatment increases with increasing pollutant concentration [15].

![Figure 4. Effect of RB5 dye concentration to removal efficiency (Constant H_{2}O_{2}; 250 ppm, Fe^{2+} 40 ppm)](image)

As a result of the optimization performed, the conditions that give the maximum color removal efficiency are shown in Table 3. A verification experiment was conducted for conditions determined and the color removal efficiency was obtained as above 99%.
Table 3. Optimum removal conditions for RB5 using FO process (Constant temperature 30°C)

<table>
<thead>
<tr>
<th>Dye Concentration, ppm (X₁)</th>
<th>pH (X₂)</th>
<th>Fe²⁺ doses, ppm (X₃)</th>
<th>H₂O₂ doses, ppm (X₄)</th>
<th>Color Removal, %</th>
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References

Deposition and Fate of Arsenic and Boron in water and sediments of streams in Neogene Emet-Hisarcık basin and downstream areas (Turkey)

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ABSTRACT

The concentration of arsenic (As) and boron (B) in a stream system influenced by historic boron mining in north-western Turkey was investigated. Water and sediment samples were obtained from both upstream and downstream parts of Emet-Hisarcık boron basin. The As and B levels varied from 5 - 1139 ug/L and 0.2 -269 mg/L, respectively in stream waters. Meanwhile, the concentration of As and B in stream sediments varied from 2 to 2759 mg/kg and 9758 - 61080 mg/kg, respectively. Upstream parts of the basin exhibited major As and B input routes from mine drainages. Moreover, significant input routes for As are also attributed to inflows from geothermal waters. Consequently, the trend in total As and B concentration in the upper basin depended on the locations of sampling points relative to the boron mining sites. The hydrodynamics of the stream reach influenced both As and B levels in sediments, as lower patterns were observed in regions of rapid stream velocity compared to areas of low stream velocity, even if major pollutant input routes existed.

Key words: Arsenic; Boron; Pollution

1. Introduction

Arsenic is a toxic inorganic chemical whose exposure to humans mainly occurs from the ingestion of As contaminated water and food (Rahman et al., 2009). The World Health Organization (WHO) guideline value for arsenic is 10 µg/L. Arsenic is a constituent of over 300 minerals and is commonly found in non-ferrous ores such as copper, lead, zinc, gold and uranium. Anthropogenic activities such as use of arsenical pesticides, wood preservatives and ore smelting may also release arsenic directly to the environment (Choong et al., 2007). On the other hand, boron is an easily soluble inorganic element. Typical boron concentrations in low-saline ground water and rivers is < 0.1 mg while saline water may show high boron concentrations of up to several tens of mg/L (Wyness et al., 2003). Sources of boron contamination in water may be anthropogenic such as sewage effluents, boron enriched fertilizers and land-fill leachates or geogenic such as water-rock interaction, sea water encroachment, mixing with fossil brines or hydrothermal fluids (Vengosh et al., 1999). Boron is toxic to sensitive crops (such as mango, avocado, citrus fruits) if present above a certain threshold (> 0.75 mg/L) in irrigation water (Sutcu, 2005). The Emet-Hisarcık basin contains major colemanite and ulexite borate deposits. Some borate minerals such as colemanite and gypsum contain extremely high As levels (Dogan and Dogan 2007). Several As and B rich thermal waters and springs are also reported the area. In this study, the distribution of arsenic and boron in water and sediment of Emet-Hisarcık basin and downstream areas were analysed in to understanding the As and B distribution and identification of the anthropogenic input routes.
2. Methodology

2.1 Study Area and sampling

The Neogene Emet-Hisarcık basin lies west of Turkey, between 39°0'0” to 40° 0'0” North latitudes and 28°0'0” to 30°0'0” East longitudes. The climate in the basin is mainly between the Mediterranean and Black Sea climates, the summers are dry and hot whereas the winters are cold. The annual precipitation in the catchment ranges between 40 mm and 65 mm with the maximum precipitation recorded in winters. Twenty-nine sample points (Figure 1) designated by GPS (GARMIN GPS eTrex 30x) were used for this study. The water samples were collected in spring (March), and autumn (October) to cater for the different hydrological conditions of the seasons. The collected water samples were analyzed for pH, water temperature, dissolved oxygen (DO), arsenic, boron, conductivity, and total dissolved solids (TDS). The analyses on temperature, pH, dissolved oxygen, and conductivity were performed in-situ using a “Mettler Toledo Seven Go” device. Total arsenic and boron concentrations were determined by Inductively Coupled Plasma - Optical Emission Spectrophotometer (ICP-OES, Optima 7000 DV, PerkinElmer, USA). Prior to analysis, water samples were filtered through 0.45µm filter. Surface sediment samples (top ~ 2 cm) were collected using a plastic spoon and subsequently sealed in polyethylene bags. The collected sediments were dried at 105°C ± 2°C for 48 hours and ground to powder using a mortar and pestle (< 100µm). 0.25 g of each sediment sample was microwave digested in Teflon vessels with a mixture of HNO₃, HF, HCl acid and H₂O₂. The volume of digestate was raised to 50 ml by ultra-pure water and subsequently filtered through Whatman filter paper No. 1.

![Figure 1: Location of sampling points used in this study.](image-url)
3 Results and discussion

3.1 Properties of the sediments and water

The measured values of As and B in the water and sediments samples is presented in Table 1. As contents of both the water and sediment samples did not show any significant variations between March and October (one-way ANOVA, \( p < 0.05 \)). However, statistically significant differences for both boron and arsenic existed between the downstream and upstream points. The pH of the water samples fluctuated from 6.79 - 9.47, showing neutral to slightly basic properties. One of the most important parameter in water quality assessment is dissolved oxygen (DO) as it affects biota. DO levels ranged from 3.17 - 11.3 and 3.9 - 9.2 mg/L for March and in October, respectively. In urban settlements, levels of DO were < 5 mg/L, due to discharge of untreated domestic wastewaters.

Table 1. Average arsenic and boron levels at sampling points for March and October

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<tr>
<th>POINT</th>
<th>March</th>
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<th>October</th>
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<tr>
<td></td>
<td>Sediment samples (mg/kg)</td>
<td>Water Samples</td>
<td>Sediment samples (mg/kg)</td>
<td>Water Samples</td>
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<td>As(ug/L)</td>
<td>B(mg/L)</td>
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<td>88060</td>
<td>371.6</td>
<td>28.29</td>
<td>6.57</td>
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3.2. Total arsenic and boron in water and sediments

Total dissolved As levels in the water column ranged from 5 - 1139 µg/L. The arsenic concentration ranged from 2 to 2759 mg/kg in digested sediment samples. The average As concentration in water samples in most of sites exceeded the WHO limit (10 µg/L). The highest As concentrations appeared at tributaries G1 and H1, suggesting a pollution origin. The total dissolved boron levels in the water column ranged from 0.2 to 1900 mg/L. The boron concentration in digested sediment samples was 9758 - 61080 mg/kg. Previous
Studies also revealed high arsenic and boron concentrations in water resources of Mustafakemalpaşa catchment, especially around boron deposit areas of Kütahya-Emet, Hisarcık, Eskişehir-Kırka and Balıkesir-Bigadiç (Gemici et al., 2008; Çolak et al., 2003). Prolonged consumption of water contaminated with arsenic may cause internal cancers, the WHO guideline for As in drinking water is 10µg/L. Boron mainly occurs as orthoboric acid in most volcanic spring waters and as borate minerals such as borax (Na₂B₄O₇.10H₂O), colemanite (Ca₂B₈O₁₁.5H₂O) and ulexite (NaCaB₅O₉.8H₂O) (Gemici, 2008). The existing borate deposits in the region are mined by open pit and underground mines. It is also worth noting that most of the thermal waters in Western Turkey are enriched with As concentrations ranging from 1 - 1419.8 µg/L. This high arsenic content is attributed to deep water circulation from a deeply seated magma body. Therefore, water-rock interaction is another important source for arsenic. Also, other researchers reported that the dissolution of ferromanganese minerals within the Late Miocene sediments in Western Turkey is partly responsible for the arsenic pollution (Baba and Sozbilir, 2012). Geogenic sources such as geothermal discharges, leaching of rocks among others may cause boron pollution in the environment. In addition, anthropogenic sources of boron pollution may include municipal wastewaters, and industrial residues, boron pesticides and fertilizers among others (Dotsika et al., 2006). It is reported that over 70% of the world boron reserves are in Turkey with major deposits in Kütahya province in northwestern turkey. Emet also hosts the words biggest colemanite-probertite deposit (Helvacı, 2015).

3.2 Spatial Variation of Arsenic and Boron in Emet-Hisarcık basin and downstream areas

Arsenic and boron were determined as the predominant pollutants in the study area at large. Figure 2 and Figure 3 show the variation of arsenic and boron pollution, respectively along the stream reach. The most upstream points E1(0 km) and E2 (11km) showed B and arsenic pollution below the WHO guideline. As the stream passes through Hisarcık boron mines, and Hisarcık and Emet settlement area at sampling points E3 (14.3 km), E4 (17.7 km), and E5(20.9 km), an increase in both arsenic and boron pollution starts to occur. Another extremely high concentration for both arsenic and boron is seen by the peak at point E7 (33.1 km), the arsenic pollution thereafter rapidly drops possibly due to dilution and absorption and then maintains fairly constant concentration downstream until confluence with Orhaneli where the arsenic pollutions are diluted and drop to variation of about 30-50 µg/L in Mustafakemalpaşa stream. Similarly, after point E7 (33.1 km), the boron pollution sinuates along Emet stream until confluence with Orhaneli stream where it shows a constant trend.
Generally, both As and B exhibited lower patterns in areas of high stream velocity compared to areas of low stream velocity, even if major pollutant input routes existed. This could be because spatial distribution of dissolved stream pollutants is largely influenced by not only their sources, but also the hydrodynamic conditions of the stream reach (Wang et al., 2015).

The findings of this study are in agreement with those in literature. Benzer et al., 2017 reported the arsenic levels of Emet stream as 137 - 1002 μg/L and also indicated boron levels of 2421-14490 μg/L. We noted the background value for As to be > 50 times that of upper continental crust (UCC). Whereas background values for B was over 5 times greater than their UCC values. This implies that these pollutants are associated with the
geochemistry of the basin, although human activities such as mining may accelerate their dissolution into streams.

Reference


Abstract

In this study, Pd/Fe bimetallic nanoparticles (Pd/FeNPs) were biosynthesized by aqueous lemon (Citrus limon (L.) Burm. f.) leaves extract as a reducing agent and were characterized by SEM analysis method. And then, Pd/FeNPs were utilized as a common heterogeneous catalyst for both in situ H$_2$O$_2$ synthesis by formic acid decomposition in the presence of oxygen and heterogeneous Fenton-like decolourisation of Basic Red 46 (BR 46) and Direct Red 23 (DR 23) azo dyes. In order to determine the decolourisation efficiency of heterogeneous Fenton-like reaction which was carried out by in situ H$_2$O$_2$ synthesis, the effects of reaction parameters such as, the concentration of formic acid, initial pH of dye solutions, initial dye concentrations and catalyst concentration were investigated for both dye decolourisation processes. Consequently, Pd/FeNPs displayed high decolourisation performances for BR 46 and DR 23 in the range of 25 – 200 mg/L BR 46 concentration and in the range of 25 – 75 mg/L DR 23 concentration.

1. Introduction

In recent years; the wastewater treatment methods are called as Advanced Oxidation Processes (AOPs), including homogeneous Fenton reaction (Fe(II)/H$_2$O$_2$), photo-Fenton reaction (Fe(II)/H$_2$O$_2$/UV), ozonation (O$_3$), wet peroxide ozonation (O$_3$/H$_2$O$_2$), H$_2$O$_2$/UV, heterogeneous Fenton-like processes and photocatalytic (TiO$_2$/UV and ZnO/UV) processes have attracted considerable attention for the removal of toxic and carcinogenic organic/inorganic pollutants from water sources. Heterogeneous Fenton-like reaction is one of the popular advanced oxidation processes. Hydrogen peroxide (H$_2$O$_2$) is the most preferred oxidizing agent because of its environmental friendliness, rapid and easy formation of hydroxyl radicals for degradation of contaminants in heterogeneous Fenton-like reactions. However, the problems such as, the use of hydrogen peroxide is much higher than which is converted into hydroxyl radicals during the reaction due to the hydrogen peroxide is fed to the system in bulk, the cost of commercial hydrogen peroxide is expensive, difficulties in synthesis method, danger of transport and storage, affect the process negatively. Therefore, the indirect synthesis of H$_2$O$_2$ catalytically in the reaction medium without adding H$_2$O$_2$ from the outside (in situ hydrogen peroxide synthesis) offers an advantage in avoiding problems caused by unnecessary use of H$_2$O$_2$ in the heterogeneous Fenton-like reactions. In this method which is called as in situ H$_2$O$_2$ synthesis; the catalytic decomposition of the organic compounds such as formic acid, hydrazine hydrate and hydroxyl amine etc., which have substituted hydrogen in their structure and mostly used for hydrogen production, leads to hydrogen gas generation and H$_2$O$_2$ can be synthesized by the reaction of hydrogen and oxygen added in reaction media [1, 2].
In this study, Pd/Fe bimetallic nanoparticles will be biosynthesized as a catalyst by aqueous lemon leaves extract as a reducing agent for both in situ H₂O₂ synthesis and the decolorisation of Basic Red 46 (BR 46) and Direct Red 23 (DR 23) azo dyes with heterogeneous Fenton-like reactions.

2. Materials and Methods
2.1. Green Synthesis of Pd/Fe bimetallic nanoparticles

The lemon leaves were firstly washed with distilled water and then air-dried at ambient temperature. For the preparation of extract, 10 g of dried leaves were boiled in 500 mL of distilled water in a beaker under continuously stirring for 60 min. For green synthesis of Pd/Fe NPs, 0.5 g of FeSO₄·7H₂O and 0.1 g of PdCl₂ were dissolved in 60 mL aqueous extract of the lemon leaves at 60 °C under vigorous stirring. Then, a solution of 1.0 M Na₂CO₃ was added dropwise to the mixture to obtain alkaline pH while changing the color to dark brown. After being stirred again for 3 hours at the same temperature, a suspension was formed which gave precipitate of Pd/FeNPs on centrifugation at 4000 rpm and the obtained nanoparticles were washed with distilled water, respectively, and then dried at 105°C in an oven [3].

2.2. Heterogeneous Fenton like decolourisation experiments with in-situ-generated H₂O₂

In-situ generation of hydrogen peroxide was performed by formic acid decomposition and O₂/air in the batch system. Heterogeneous Fenton like decolourisation experiments with in situ H₂O₂ generation were conducted in Erlenmeyer flasks (250 mL) containing 100 mL of dye solutions in a shaker that was adjusted 25°C of temperature and constant shaking rate. In the experiments, 0.1 g of Pd/Fe NPs, except for catalyst concentration experiments, was added to solutions containing 50 mL of 500 mM formic acid and 50 mL of dye solutions at known initial dye concentrations and they were agitated in the water bath at constant temperature. Initial pH of dye solutions was adjusted by 0.1 N HCl or 0.1 N NaOH solutions. Oxygen/air was passed into the reaction medium with aquarium pumps for 2 hours and then air was turned off. Subsequently, dye concentrations were monitored by sampling at regular time intervals and analyzed by using the UV–vis spectrophotometer at the wavelength of 530 and 507 nm for BR 46 and DR 23, respectively.

3. Results
3.1. The characterization of green synthesized Pd/Fe bimetallic nanoparticles

The crystalline structure of Pd/FeNPs was confirmed with XRD measurements. According to XRD analysis results, the presence of palladium and iron was confirmed in the structure of Pd/FeNPs (figure not shown). In order to identify the structure of catalyst in detail; SEM, EDX and FT-IR analysis will be also carried out.

3.2. Influencing Factors of Heterogeneous Fenton-like Decolourisation of Basic Red 46 and Direct Red 23 with in-situ-generated H₂O₂

3.2.1. Effect of initial pH

The pH value is one of the important parameter for the decolourisation/degradation of organic pollutants, due to its effect on the generation of H₂O₂ from the reduction of O₂ by catalyst and the in-situ generation of •OH from the decomposition of H₂O₂ by Fe (III) ions. Moreover, it is generally reported that a lower initial pH value provides the generation
of •OH radicals and results in the higher removal efficiency of pollutant in the Fenton-like decolourisation processes. The initial pH effect on the heterogeneous Fenton-like decolourisation of BR 46 and DR 23 with in-situ-generated H$_2$O$_2$ is presented in Figure 1. As seen from Figure 1, the final removal efficiency of BR 46 was 97.56% after 10 h reaction time and 0.5 g/L catalyst concentration, at initial pH of 3.0 and the removal efficiencies of BR 46; decreased slightly when the pH of solution was increased. On the other hand, according to Figure 1, the final removal efficiency of DR 23 was 85.84% after 10 h reaction time and 1 g/L catalyst concentration, at initial pH of 3.0 and the removal efficiency of DR 23; was 80.75%, 76.06% and 74.23% at initial pH of 4.0, 5.0 and 6.0, respectively. As a result, initial pH 3.0 was proved to be more suitable for Fenton-like decolourisation of BR 46 and DR 23 by Pd/FeNPs/O$_2$ process.

![Figure 1](image_url)  
**Figure 1.** The effect of initial pH (C$_o$=25 mg/L, C$_{Fe}$= 500 mM, X$_o$=0.5 g/L (BR 46), X$_o$=1 g/L (DR 23), T=25°C, time=10 h)

### 3.2.2. Effect of catalyst concentration

The effect of catalyst concentration on the dye decolourisations in the Fenton-like process with in-situ-generated H$_2$O$_2$ is presented in Figure 2. As seen from Figure 2, with the Pd/FeNPs concentration increased from 0.5 g/L to 3 g/L, the BR 46 decolourisation efficiency increased from 38.83% to 94.74%. This was mainly owing to the increasing amount of active sites for the reduction of O$_2$ to produce more reactive species such as H$_2$O$_2$ and •OH. So, the 3 g/L of catalyst concentration was selected optimum in order to achieve the high BR 46 color removal efficiency. When the Pd/FeNPs concentration increased from 0.5 g/L to 2 g/L, the DR 23 decolourisation efficiency increased from 60.62% to 90.74%. However, the decolourisation degree was slightly decreased when the catalyst concentration increased from 2.0 to 3.0 g/L, which was may be attributed to the percentage of •OH scavenged by Fe(III) through undesirable reaction [4]. Thus, the optimum Pd/FeNPs concentration was 2 g/L for DR 23 decolourisation.
Figure 2. The effect of catalyst concentration ($C_o=25$ mg/L, $C_{FA}=500$ mM, pH=3.0, $T=25^\circ$C, time= 10 h (DR 23), time= 2 h (BR 46))

3.2.3. Effect of formic acid concentration

In-situ generation of H$_2$O$_2$ was produced through the reaction of formic acid and O$_2$. Formic acid was used as a source of hydrogen to produce H$_2$O$_2$ in this study. The researchers reported that, formic acid can be decomposed over Pd to CO$_2$ and H$_2$ which further reacts with O$_2$ to produce H$_2$O$_2$ [5]. Therefore, the optimum formic acid concentration should be determined, due to, it is related to the amount of hydroxyl radicals produced during the reaction. The effect of formic acid concentration for BR 46 and DR 23 decolourisation was presented in Figure 3. According to Figure 3, the highest decolourisation percentage of BR 46 was obtained in 1000 mM formic acid concentration and 500 mM formic acid concentration was optimum for DR 23 decolourisation. The reason of decreasing the decolourisation percentage of DR 23 during in situ generation of hydrogen peroxide high concentration of formic acid may be due to the deactivating the catalyst to decolourisation of DR 23 by avoiding dye molecules to be exposed to the generated hydrogen peroxide or by consumption of generated H$_2$O$_2$ or •OH by formic acid itself. Therefore, 500 mM was found to be favorable for DR23 decolourisation.

Figure 3. The effect of formic acid concentration ($C_o=25$ mg/L, $X_o=0.5$ g/L, pH=3.0, $T=25^\circ$C, time= 5 h)
3.2.4. Effect of initial concentration of BR 46 and DR 23

The effect of initial dye concentration on BR 46 and DR 23 decolourisation was presented Figure 4-a and Figure 4-b, respectively. The results showed that the removal efficiency of BR 46 was 94.70%, 95.64%, 95.12% and 95.71% when BR 46 concentration was 25, 50, 100 and 200 mg/L, respectively after 5 h. Also, the removal efficiency of DR 23 was 90.47%, 90.38%, and 85.18% when DR 23 concentration was 25, 50, and 75 mg/L, respectively after 10 h. The a bit lower removal efficiency of DR 23 at higher initial dye concentration, was due to more DR 23 dye was available in the solution for oxidation. Also, as seen from Figure 4-a and b, catalyst blank experiments (without catalyst, bubbling O₂ in HCOOH added dye solutions) carried out. When O₂ passed into the reaction medium, no detectable activity towards dye decolourisations were observed. Moreover, the adsorbent property of Pd/FeNPs was investigated in the same experimental conditions but the absence of formic acid and H₂O₂. These adsorption experiments showed that, almost no colour removal percentages were found both two dyes. Therefore, it was believed that, the decolourisation mechanism of both dyes depends on the in-situ generation of H₂O₂ and also, Fe and Pd played important roles in the synergistic effect, that is, Pd nanoparticles worked in in-situ H₂O₂ generation by formic acid decomposition and Fe nanoparticles worked in decompose H₂O₂ for generating and •OH radicals to decolourisation of BR 46 and DR 23.

Moreover, heterogeneous Fenton like decolourisation experiments of BR 46 and DR 23 with in-situ-generated H₂O₂ were monitored by UV-vis spectral analysis. Changes in the absorption spectrum of dye were monitored in Figure 5-a and Figure 5-b, respectively. Also the progress of the decolourisation was given in the inset of the Figure 5-a and 5-b. According to Figure 5-a and b, in the visible region, the broad bands at 530 nm and 507 nm result from the conjugated π system, linked by the two azo groups which are responsible for the colour of BR 46 dye and DR 23 dye, respectively. Consequently, with the increase of the reaction time, the adsorption peaks gradually declined and approximately disappeared, which suggested that the chromophoric group (N=N group) in the dye molecular structures were broken as well as conjugated system and eventually the BR 46 and DR 23 molecules were decolourized.
Consequently, the synthesized catalyst displayed excellent performances for BR 46 and DR 23 removal by in-situ generation of hydrogen peroxide and heterogeneous Fenton-like catalytic reaction.

References


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

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

Uncontrolled struvite formation (magnesium ammonium phosphate) has been a big issue in wastewater treatment plants, most commonly in anaerobic digesters or downstream dewatering facilities. On the other hand, the use of struvite in agriculture as a slow release phosphorus fertilizer is a promising alternative for sustainable management of phosphorus especially while considering the phosphorus depletion. To achieve efficient struvite precipitation prior to anaerobic digestion, it is a necessity to release nutrients from bacterial cells as initial step. Alkaline fermentation is an effective and feasible sludge solubilization technology. By fermentation, VFA production can be achieved as a valuable carbon source; besides, sludge reduction and nutrient releases can be accomplished (Yuan et al., 2016). This paper represents the mesophilic alkaline fermentation studies for the nutrient recovery from excess sludge.

Methodology

Fermentation

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

\[
\text{Release(\%)} = \left( \frac{\text{soluble COD,P-soluble COD,P_{initial}}}{\text{particulate COD,P_{initial}}} \right) \times 100
\]  
(Eq.1)

MAP Production

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

Results & Discussion

Long-term fermentation studies between 5 and 23 days were performed to determine the optimum conditions for nutrient release. As shown in Figure 1.1, mesophilic fermentation at pH:10 showed the highest phosphorus release. Higher temperature slightly enhanced the phosphorus release also in pH:9 and pH:8 experiments without any significant differences (p:0.121 and p:0.275), thus low mesophilic temperature might be more advantageous due to energy cost for heating. Also, as mentioned by Li et al. (2014), phosphorus loses according to Ca₃(PO₄)₂ may occur at higher temperatures. Decreases in orthophosphate concentration were appeared as fermentation continues, especially in low mesophilic conditions possibly due to phosphorus precipitation. Therefore, short fermentation periods even as one day might be another cost saving and effective option. Besides phosphorus, ammonia concentration of the sludge increased during the fermentation studies. The highest
ammonia increase was observed after seven-day mesophilic fermentation at pH:10; ammonia-nitrogen concentration increased from 1.47 to 20.65 mgNH₄-N/gMLSSinitial. Meanwhile, mesophilic fermentation experiments for all studied pH values were more effective than ambient temperature fermentation. The results may indicate the preventing of struvite precipitation during fermentation by higher temperatures.

During the fermentation experiments, phosphorus fractions were also studied (Figure 2). As shown, a remarkably decrease in particulate phosphorus was observed after first day of fermentation and the fractions were slightly influenced then. The results drove short term fermentation forward once again, for phosphorus release. Besides, organic phosphorus releases were also observed in mesophilic fermentation as a result of cell lysis.
As mentioned by Ma et al. (2016), alkaline conditions enhance the sludge disintegration; accordingly, highest COD release was also observed in mesophilic pH:10 fermentation. Furthermore, higher temperature promoted the higher COD releases and MLVSS solubilizations as reported by Li et al. (2014). As shown in Figure 3.1 and 3.2 both COD release and MLVSS solubilization rates accelerated as fermentation continues due to increase in available substrate concentration for microbial activity as a result of sludge disintegration.

**Figure 2.** Phosphorus fractions during fermentation studies.
Figure 3.1. COD releases and 2. MLVSS solubilizations during fermentation.

Alkaline pH conditions promote the VFA production by increasing hydrolysis rate so that soluble substrates for acidification and inhibiting the activity of methanogens (Ma et al., 2016, Chen et al. 2007). As shown in Figure 4, VFA production was greater in pH:10 fermentation than pH:8 at 30°C (Figure 4) in line with the results of Gao et al. (2011). VFA production decreased with further fermentation time in pH:10 experiments and stabilized in pH:8 fermentation. This might be the result of the inhibition of acidogenic bacteria by alkaline condition as mentioned by Chen et al. (2007). Besides, a slight VFA production was also observed in ambient temperature experiments after more than 7-day fermentation periods. (Figure not represented).
Conclusion
In the scope of the study, sludge fermentation experiments were run with different pH conditions (8, 9 & 10) and temperatures (30°C & room temperature). Stronger alkaline conditions showed higher nutrient release, sludge solubilization and reduction and VFA production. While higher temperature enhances the VFA production, difference was not significant in terms of nutrient release. Besides, short term fermentations even as one day were determined as sufficient for phosphorus release and optimum in terms of operational cost and feasibility.

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

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Keywords: Pervaporation, Membrane, Poly (dimethylsiloxane), Bio-alcohol, Fermentation

Abstract

The pervaporation separation method is considered to be a promising technique for bio-alcohol recovery from fermentation broths. Alcohol produced from biomass, called bioalcohol, is an important renewable energy source. In this study, for the separation of bio-alcohol from fermentation broth by pervaporation, the pristine polydimethylsiloxane (PDMS) and the PDMS/SiO$_2$ mixed matrix membranes (MMMs) with nanoparticle contents of 1 wt % were prepared with a novel preparation method, and characterized by scanning electronmicroscopy (SEM), Fourier-transform infrared (FTIR) and thermal gravimetric analysis (TGA). Sorption studies were performed at 30, 40, 50°C, while permeation studies were performed at 30°C for pure butanol, ethanol and water. Experimental results indicated that the nanoparticle incorporation into the polymeric matrix enhanced the membrane performance, and the prepared membranes can be used for bio-alcohol separation during fermentation process.

1. Introduction

In general, separation methods used for the separation and purification of bio-alcohols are distillation, adsorption, extraction, pervaporation, reverse osmosis or gas stripping methods (Oudshoorn et al., 2009). As energy issues have become increasingly important, there has been growing interest towards separation processes with low energy consumption (Kuhn et al., 2009). There has been an increasing attention for alcohol-permselectivity pervaporation in bio-alcohol production due to the advantages of low energy consumption. In recent years, with the increasing concerns of energy shortage, alcohol fuel (mainly including ethanol and butanol) produced from biomass has gained great attention as an renewable alternative for fossil energy (Zhao and Jin, 2017). Pervaporation (PV) has been considered as one of the most active and promising areas in membrane technologies for separation. In the PV process, the membrane matrix has an important role on separation efficiency (Roy and Singha, 2017).

Production of butanol may be made by a fermentation process called ABE (acetone, butanol, ethanol), carried out mostly by bacteria Clostridium acetobutylicum. During alcohol separation, the membrane must be hydrophobic since organic components from the fermentation broth are transported. PDMS-based membranes are commonly used for the pervaporation separation of organic compounds (Kaminski et al., 2011).
In addition, mixed matrix membranes (MMMs) or composite membranes consisting of inorganic and polymeric phases are also used, which improve separation efficiency by linking via van der Waals forces and covalent or hydrogen bonds (Siddique et al., 2014). In this study, pristine PDMS membrane and a mixed membrane matrix comprising of PDMS/SiO$_2$ with nanoparticle of 1 % as weight were used for bio-alcohol separation. Moreover, the membranes were characterized by scanning electron microscopy (SEM), Fourier-transform infrared (FTIR) and thermal gravimetric analysis (TGA).

2. Materials and Methods

2.1. Materials

Two-component PDMS (RTV 655 A/B) elastomer kit was purchased from GE Silicones (NY, USA). Chloroform, ethanol and butanol were obtained from Merck (Darmstadt, Germany). The silicon dioxide (SiO$_2$) nanoparticles coated with silane (average particle size 16 nm, specific surface area 150-550 m$^2$.g$^{-1}$) was purchased from Nanografi Nano Technology (Ankara, Turkey).

2.2. Preparation of Mixed Matrix Membranes

For better dispersing the silicon dioxide nanoparticles (NP) in the PDMS(A) matrix, first a desired amount of silicon dioxide nanoparticles were dispersed into the solvent (chloroform) in an ultrasonic water bath for 1h. Then, the curing agent (B) was added and mixed at mechanical stirrer for 2h. In the meantime, viscous PDMS(A) was diluted in chloroform with a mechanical stirrer for 1h. The weight ratio of PDMS(A) to B was maintained at 10:1. After PDMS(A) to NP/B mixture was added. They were all mixed together for 1h. The mixture (A/B/NP) was held under vacuum for 2h to remove the air bubbles. The mixture was poured onto glass Petri dishes. Then, the membranes were placed in a oven for 4 h at 65°C to ensure PDMS polymerization through thermal curing.

2.3. Characterization

The morphology of the prepared membranes was examined by SEM. Thermal degradation analyses were that used to obtain weight loss of membrane data for the thermal degradation FTIR spectroscopy was used to monitor the incorporation of the SiO$_2$ in the PDMS Matrix and to verify the final chemical structure of the polymer.

2.4. Determination of Swelling Degree

The swelling degree of the mixed matrix membranes were measured by immersing the polymer films in pure butanol, ethanol and water at 30, 40, 50°C. The films were taken out, then quickly wiped with filter papers and periodically measured until constant weight. The membrane swelling degree (SD) was calculated by using the following equation:

$$SD\% = \frac{W_s - W_d}{W_d} \times 100$$

where $W_d$ and $W_s$ are the weights of the dry and swollen films, respectively.
2.5. Pervaporation experiment

The pervaporation experiments were performed using a membrane cell with an effective area (A) of $2,296 \times 10^{-3} \text{ m}^2$ was connected with three cold traps, followed by a vacuum pump. The membrane cell was heated by a heater and a peristaltic pump was used for recirculation of liquid feed. The pressure on the permeate side was kept below 1 mmHg during the experiment. The permeate was sampled from the cold traps in a liquid nitrogen bath at intervals to determine. The permeate flux was calculated as:

$$J = \frac{W}{A \cdot t \cdot l} \frac{1}{100}$$

where the permeate flux ($J$) was obtained by weighing the permeate product collected in a cold trap ($W$) for a given time ($t$). $l$ membrane thickness and the thickness of the membrane used in the tests was normalized to 100 μm.

3. Results

3.1. FTIR analysis

The FTIR spectra of the pristine PDMS and the SiO₂-filled PDMS membranes in the 650-4000 cm⁻¹ region are shown in Fig. 1. The pristine PDMS and the SiO₂-filled PDMS membranes show similar characteristic bands: the peaks at 790 and 1260 cm⁻¹ are assigned to Si-C stretching and symmetric C–H bending (Johnson et al., 2013). Transmission peaks at 2960 cm⁻¹, 2905 cm⁻¹ and 1410 cm⁻¹ correspond to the asymmetric C-H stretching, symmetric C–H stretching and asymmetric C-H bending, respectively (Gaboury et al., 1992). The bands observed at 1000-1100 cm⁻¹ are assigned to Si–O–Si stretching of PDMS. The characteristic band at 843 is corresponding to C–H (–CH₂) rocking (Silva et al., 2016).

Figure 1. The FTIR spectra of the pristine PDMS and 1 % SiO₂-filled PDMS membranes.
3.2. Morphology of SiO2-filled PDMS membrane

In MMMs, the morphology of dispersed phase strongly influences the separation properties. According to SEM results (Fig. 2), the nanoparticles of SiO2 have relatively uniform dispersion in PDMS matrix.

![Figure 2. Cross-sectional SEM images of 1 % SiO2 filled-PDMS membrane](image)

3.3. Thermal stability of pristine PDMS and SiO2-filled PDMS membranes

Thermal gravimetric analysis of the pristine PDMS and the SiO2-filled PDMS membranes are shown in Fig. 3. The weight loss is lower in 1 % SiO2-filled PDMS membrane. The filled of SiO2 into the polymer matrix have enhanced the stability of PDMS. It observed that mixed matrix membranes decomposed at temperature 800°C, while pristine PDMS decomposed at about 500°C. The improved thermal stability is due to physical interaction only (Yi et al., 2010).

![Figure 3. TGA curves of the prepared membranes.](image)

3.4. Sorption results
The sorption behaviors were tested with and without SiO$_2$-filled PDMS membranes in pure butanol, ethanol and water at different temperatures. The results indicate that the sorption amount increases with the increasing of temperature for both cases as the polymer chain mobility increases (Fig. 4).

![Figure 4. Effects of temperature on sorption pristine(a) and 1% SiO$_2$-filled (b) PDMS membranes.](image)

The sorption percentages of butanol and ethanol are apparently higher than water sorption due to chemical affinity between PDMS and alcohols. Also, it is clear that PDMS membranes preferentially sorb butanol, and the amounts of butanol sorption in 1 wt % SiO$_2$-filled membrane are higher than the sorption values obtained in pristinePDMS membrane at all temperatures. As a result, 1% SiO$_2$-filled PDMS membrane prepared can be used effectively for bio-alcohol recovery by pervaporation.

### 3.5. Permeation results

Permeation studies were performed at 30°C for pure butanol, ethanol and water. As can be seen from Fig. 5, PDMS-SiO$_2$ mixed matrix membranes led to pure water, ethanol and butanol permeate fluxes of 132, 782 and 806 g.m$^{-2}$.h$^{-1}$, respectively.

![Figure 5. Pure water, ethanol and butanol fluxes of 1 % SiO$_2$-filled PDMS membrane at 30°C](image)

The separation of pure butanol, ethanol and water by the membranes was carried out initially to evaluate the membrane permselectivity, which was found to follow the order of
butanol>ethanol>water. The membranes were shown to be prefentially permeable to organic compounds rather than water. Alcohols show a high affinity for PDMS. The PDMS-SiO₂ mixed matrix membranes prepared in this study could be a niche application for alcohol recovery from the fermentation broth.

4. Conclusion

This study has showed a great separation potential and potentially huge reduction in energy cost offered by the membrane-based process makes it a serious candidate for water-ethanol-buthanol separation at large scale fermentation applications.

Acknowledgement

The authors would like to acknowledge Berk Tırnakçı for helping to prepare the membranes.

References


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

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Abstract

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

Abstract

Processing of the liquid phase remaining after nutrient recovery from source separated urine is an important issue. Possibility of using anaerobic treatment for this purpose is considered in this work as an option. To start this investigation, adaptation of an anaerobic biomass to urine, which is highly saline and has high nutrient and COD content, was observed for over two months. 75% and 60% of removal could be achieved for soluble and total COD, respectively, together with minor amounts of NH$_4^+$ release into the liquid phase. The amount of CH$_4$ produced was calculated from COD removal as 1.3 CH$_4$/day and 0.24 l CH$_4$/l urine.

1. Introduction

One of the most effective ways of recycling nutrients in domestic wastewater is segregation of human urine at the source and processing it further to produce fertilizers to be returned to the food chain. Human urine is a nutrient rich stream containing 80% of nitrogen, and 50% of both phosphorus and potassium in domestic wastewater, in addition to highly concentrated organic matter content, and high salinity (Beler-Baykal, 2015). Ion exchange/adsorption is one of the successful methods of recovering nutrients from urine which may be recycled to agricultural use (Beler-Baykal et al, 2004, 2011; O'Neal & Boyer, 2013; Sendrowski & Boyer, 2013; Caspersen & Ganrot, 2018). This may be done through contacting urine with clinoptilolite (a natural zeolite which is also used as a soil conditioner) upon which nutrients are concentrated, leaving a liquid residue which has a high COD content, typically over 4000 mg COD/l, and high salinity over 20000 µS/cm (Kocaturk & Beler-Baykal, 2012). This residual liquid phase has to be treated before disposal for environmental protection. COD concentrations of this residue are fit for anaerobic processes, which may act not only to treat the organic fraction but also can generate biogas that may possibly be used for recovering energy. Yet the high salinity of the liquid phase is a challenge which needs attention.

There are very limited studies in the literature where anaerobic processing is employed to handle organic matter in human urine. Previous studies in the literature used urine only in co-digestion rather than using it by itself to feed an anaerobic reactor. In the work by Kpat-Konan et al (2013), urine was used as a co-substrate in anaerobic biodigestion of manioc wastewater to improve the biogas productivity. The results of that study revealed that addition of human urine helped to increase the biogas productivity from 14.63 dm$^3$ to 60 – 80 dm$^3$. In another work by Lavagnolo et al, (2017), where anaerobic treatment of kitchen waste in combination with brown water and yellow water (urine) was investigated, the results showed that, addition of yellow water had improved the performance of the batch
reactor systems used. This was attributed to the micronutrients present in yellow water. According to the same study the percentage of urine in the reactor was observed to be significant due to ammonia inhibition when urine percentages were high. No publications were encountered in the literature which investigated anaerobic treatment for processing/reevaluating urine as its focus.

Additionally, several pieces of work in the literature like Suschka and Grubel (2014) reported possible ammonium release during anaerobic processing. The ammonium release was attributed most probably to anaerobic hydrolysis of the organic nitrogen in the feed.

The purpose of this paper is to present the preliminary results from an Expended Granular Sludge Bed (EGSB) reactor performing anaerobic treatment to remove organic matter from urine. The main focus of this particular investigation was the adaptation of the anaerobic sludge with a feed solution of 25% fresh urine, in an attempt to adapt the anaerobic sludge from a confectionary wastewater treatment plant to highly saline urine feed. The adapted granular sludge was to be used later to handle the remaining liquid phase from the ion exchange/adsorption process, for removing the organic matter in an EGSB reactor for environmental protection, meanwhile producing biogas from this waste stream. Performance of the EGSB reactor was investigated not only for organic matter removal but also to see if anaerobic processing will have an effect on NH4+ concentrations.

Table 1 shows characteristics of fresh urine as well as the confectionery wastewater upon which the granular sludge was produced in this work. It may be observed that the pH of fresh urine falls within the range of the confectionary wastewater while the COD content is at the lower end of the range for the latter. However, conductivity and nitrogen forms in fresh urine are greater than that of their counterparts in confectionery wastewater, specifically about 35 fold for conductivity and over 45 fold for nitrogen, indicating the main challenges in this investigation.

<table>
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<tbody>
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<td>5.6 – 6.8</td>
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<tr>
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<td>14800 – 25400</td>
<td>252 - 689</td>
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<tr>
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<td>mg COD/l</td>
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<td>3400 - 6550</td>
<td>6540 - 37180</td>
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<td>Ammonium</td>
<td>mg NH4+/l</td>
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<td>780</td>
<td>0.22 – 15.4</td>
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<tr>
<td>TKN</td>
<td>mg N/l</td>
<td>5700</td>
<td>4700</td>
<td>16 - 95</td>
</tr>
</tbody>
</table>

2. Materials and Methods

Urine was collected from men’s toilet at Istanbul Technical University, Department of Environmental Engineering, originating from urinals that use flush water. The feed solution was 25% fresh urine diluted with tap water. The pH of the feed solution was controlled with hydrochloric acid to keep it at around 7.5 to maintain a suitable pH for anaerobic sludge as well as to keep the nitrogen in ammonium form.
The granular sludge to be adapted to urine feed was originally provided from the anaerobic unit of a confectionary plant treating confectionary wastewater whose characteristics are summarized in Tables 1 and 2.

The experiments were performed in a lab scale EGSB reactor that has a volume of 9.2 l, with a total height of 1.21 cm and 8.0 cm diameter of the lower column where the granular sludge is located, while the diameter of the upper part is 20 cm, which is designed for biogas collection. Two pumps were connected to the column, one for feeding the other one for circulation. The circulation pump was adjusted until the granular sludge was in suspension as it is one of the main characteristics of EGSB reactors. The EGSB reactor was fed with 5.5 l/day at a HRT of 40 hrs and OLR of 0.72 kg COD/m³d. The feeding of the column was done intermittently. 30% of the reactor volume was filled with granular sludge from the confectionary plant. The reactor was located in a constant temperature room adjusted to 35–40°C to maintain mesophilic temperature conditions.

Parameters which were monitored continuously on a daily basis were pH, conductivity, COD and N as ammonium and TKN. pH was determined by using a pH probe, and conductivity by a conductivity probe. COD was measured by Open reflux method, and nitrogen analyses as ammonium and TKN were made by using ammonium probe and Macro Kjeldahl Nitrogen method (APHA et al, 2005).

3. Results

Table 2 shows characteristics of the 25% fresh urine solution used to feed the EGSB reactor, together with those of the source of the fresh urine that it was prepared from. Characteristics of the confectionery wastewater solution are added once again to show the compatibility between the original wastewater with which the granular sludge was produced, and the feed solution used in this work. A comparison of the feed with confectionery wastewater shows that the pH was compatible with the wastewater as well as the levels recommended for anaerobic treatment as 6-8 by Khanal (2011). The COD was low, however at a reasonable level for anaerobic treatment when compared to the low end values given by Metcalf and Eddy (2004), as 1500 mg COD/l as the value preferred for a sufficient CH₄ production.

### Table 2. Characterization of fresh urine used in the experiment

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>25% Fresh urine, average</th>
<th>100% Fresh urine, average</th>
<th>Confectionery WW (Ozgun, H. et al, 2012)</th>
</tr>
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<td>pH</td>
<td>pH unit</td>
<td>7.5</td>
<td>9.3</td>
<td>3.83 – 6.48</td>
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<tr>
<td>Conductivity</td>
<td>µS/cm</td>
<td>8100</td>
<td>20000</td>
<td>252 – 689</td>
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<td>COD</td>
<td>mg COD/l</td>
<td>1200</td>
<td>4500</td>
<td>6540 – 37180</td>
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<td>Ammonium</td>
<td>mg NH₄+/l</td>
<td>906</td>
<td>3550</td>
<td>0.22 – 15.4</td>
</tr>
<tr>
<td>TKN</td>
<td>mg N/l</td>
<td>2660</td>
<td>9800</td>
<td>16 – 95</td>
</tr>
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</table>

Free ammonia and ammonium are factors that may lead to inhibition of anaerobic processes in the concentration range of 1500 – 7000 mg/l of TAN (total ammonia nitrogen) as indicated by Hejnfelt and Angelidaki (2009). Table 2 shows that concentrations of nitrogen were by far higher in urine as compared to the confectionary wastewater, however, when diluted to 25%, ammonium concentration was at an acceptable level.
Regarding salinity, 100% fresh urine has a salinity (as measured in units of conductivity) level which is about 28 fold higher of that for confectionery wastewater. Salinity inhibition in anaerobic processes was investigated by Ogata et al. (2016), to indicate that an electrical conductivity of 35000 µS/cm could decrease methane production, while an electrical conductivity of 80000 µS/cm inhibits methane and CO₂ generation as well inhibiting the degradation of organic matter. With the 25% urine feed, although there was more than 10-fold difference, conductivities were below these limits.

Under experimental conditions employed in this study, the results revealed that with 25% fresh urine, COD removal efficiency fluctuated in the first month of operation in the startup period, but stabilized thereafter as shown in Figure 1. The influent was at an average 1200 mg COD/l while the effluent was around 550 mg COD/l at the beginning, which after one month started to stabilize at a concentration of 350 mg COD/l. Tiny particles were observed in the effluent from time to time that was most probably due to biomass escaping from the column which led to higher CODs in the effluent. Based on this observation, soluble COD analysis was also made and the results have revealed that the system was reasonably successful in terms of reducing total COD concentrations from about 1200 to 440 mg COD/l with a reduction of 60%, and for soluble COD from 1100 mg COD/l to 300 mg COD/l with a reduction of 75%, as shown in Figure 1.

![Figure 1](a) COD concentrations in influent and effluent, (b) COD removal efficiencies based on total and soluble COD.

Figure 2. shows the pH values of the EGSB reactor. pH of influent was always kept at values around 7.5 to maintain a suitable pH for the anaerobic sludge used, and to be able to prevent conversion of ammonium to ammonia at higher pHs, as this study also aims to investigate the release of ammonium at the effluent of the EGSB reactor. A slight increase in pH was observed in the effluent.

The ammonium concentration in influent was within a range of 720 – 1020 mg NH₄⁺-N/l and the effluent was in the range of 820 – 1030 mg NH₄⁺-N/l. The fluctuation in the start-up period was observed to be less with ammonium concentrations as compared to that of COD. A small ammonium release was observed in the effluent at an average of 6%, which was rather low as shown is Figure 3, and that was comparable to TKN results in which the increase between the influent and the effluent was 3% at an average, as shown in Figure 4.
Figure 2. pH values of the anaerobic system

Figure 3. Ammonium concentrations in the influent and effluent

Figure 4. TKN concentrations in the influent and effluent

Figure 5. presents salinity measured as conductivity in the influent and the effluent of the EGSB reactor. The conductivity in 25% fresh urine influent solution was 8100 µS/cm, and there was a slight change at the effluent which was 8800 µS/cm as an average. Conductivity levels fluctuated also until it stabilized after almost a month from the start of the EGSB reactor, similar to the COD concentration.

Figure 5. conductivity of influent and effluent of 25% fresh urine in mS/cm

The amount of methane produced was calculated based on the COD removed per day using the assumption 0.35 l CH₄/g COD and the calculation showed that an average of 1.3 l CH₄/day will be produced from such a lab-scale system, which is equivalent to 0.24 l CH₄/l urine that makes about 0.005 kWh.

Table 3. Summary of major experimental results as averages
Table 1: Summary of Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>COD (mg/l)</th>
<th>NH$_4^+$ (mg NH$_4^+/l$)</th>
<th>TKN (mg NH$_3$-N/l)</th>
<th>pH</th>
<th>Conductivity (µS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>1200</td>
<td>906</td>
<td>2660</td>
<td>7.5</td>
<td>8100</td>
</tr>
<tr>
<td>Soluble</td>
<td>1100</td>
<td>300</td>
<td>2690</td>
<td>8.1</td>
<td>8800</td>
</tr>
</tbody>
</table>

The results obtained in this work indicate that treatment of urine using anaerobic processes is possible and that best operational conditions are to be determined for combined sorption and anaerobic processes to lead to a concurrent nutrient recovery accompanied by treatment of residual urine while possibly producing biogas, to support sustainability concepts.

### Conclusion

Following an adaptation period of two months, the EGSB reactor performance with 25% fresh urine was considerably significant in terms of removing organic matter with about 75% efficiency based on soluble COD, and 60% based on total COD. Ammonium release in this work was found to be low with 6% only. This investigation aimed to adapt anaerobic granular sludge from a confectionery industry to 25% fresh urine to make it available for further use for anaerobic treatment of the liquid residue from sorption process in which nutrients had been removed from urine, and the results provided evidence that this could be accomplished.

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Optimization of Hardness Removal with Response Surface Methodology
from High Boron Containing Wastewater Using Bigadiç Clinoptilolite

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

Abstract
In Bigadiç Etimaden boron plant, wastewater originating from boron mineral processing is
collected in wastewater dam and contains boron and hardness in high concentration. In
advanced treatment of boron from the wastewater, the hardness has a negative effect.
Therefore, the raw clinoptilolite and modified clinoptilolite with HCl and NaOH were used
to remove hardness from wastewater. The raw clinoptilolite was obtained from Bigadiç
Boron Plant. Response Surface Methodology (RSM) was used to determine the optimum
conditions for removal of total hardness and calcium hardness from the wastewater.
Clinoptilolite dosage, contact time, temperature and dilution ratio were selected as
independent variables. The equations giving the removal of total hardness and calcium
hardness were obtained through RSM and the interaction of the independent variables with
each other is illustrated by contour graphs. R² values were above 0.90. The highest removal
efficiency and adsorbent capacity were obtained by NaOH modified clinoptilolite.

1. Introduction
The boron element has many uses and is a critical parameter in terms of environment. Boron
has toxic effects on plants, animals and people if it is above the limit values in the waters
and it must be treated before discharge into environment [Wang et al, 2014; Yılmaz et al,
2005; Köse and Oksüz, 2009; Tu et al, 2010; Kavak, 2009]. There are various processes for
removal of boron from wastewater such as membrane distillation [Ozbay-Unal et al, 2018],
adsorption [Bryjak et al, 2008], ion exchange [Ozmetin et al, 2009], reverse osmosis (RO)
[Wang et al, 2018] and electrocoagulation [Isa et al, 2014] etc. Once RO is selected as boron
treatment method, the high amount of hardness in wastewater causes stratification and
clogging on RO membrane surface. Therefore, the pre-treatment of hardness must be done
before advanced treatment of boron. Other hand, the conventional pre-treatment methods increase total cost of boron removal [Duman and Ozmetin, 2014].

Zeolites are aluminosilicate minerals that contain interchangeable alkali and alkaline earth metal cations in addition to the water in the structural frameworks. The clinoptilolite is one of the most abundant natural zeolite species in the world and found in relatively large pelitic sedimentary deposits of sufficiently high purity [Gunay, 2007]. The hardness in the water is due to the polyvalent metal cations [Sawyer, 2013]. The clinoptilolite is one of the natural zeolite used to remove cations [Demir et al., 2002]. In this study, it was aimed to determine optimum conditions for the hardness removal from boron containing wastewaters by using raw and modified clinoptilolite.

2. Material and Methods
The wastewater used in the study was supplied from the wastewater dam in the Bigadiç Etimaden Boron Mineral Mining and Enrichment Plant. The characterization of wastewater is given in Table 1. In order to remove the total hardness and calcium hardness, the clinoptilolite known as abundant and cheap material in the nature was used. In the study, the raw and modified by HCl and NaOH clinoptilolite were used. In the preparation of the modified samples, the clinoptilolite was first dried, then the dried samples were weighed on a precision scale and treated with 1 M of HCl or NaOH solution for 24 hours and suspensions were filtered and dried.

Table 1. Characterization of wastewater

<table>
<thead>
<tr>
<th>pH</th>
<th>Conductivity (µS/cm)</th>
<th>Total Hardness (mg CaCO₃/L)</th>
<th>Calcium Hardness (mg CaCO₃/L)</th>
<th>Boron (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8,66</td>
<td>2137</td>
<td>658,784</td>
<td>211,68</td>
<td>602,89</td>
</tr>
</tbody>
</table>

RSM is a collection of mathematical and statistical techniques can be useful for analyzing the effects of several independent variables on the response [Birjandi, 2013]. The experiments were carried out under conditions determined by RSM. The clinoptilolite dosage, contact time, temperature and dilution ratio were chosen as independent variables of RSM and the adsorption capacity of clinoptilolite and the removal efficiency of total hardness and calcium hardness were chosen as dependent variables of RSM. The factors and levels of design are given Table 2.

Table 2. The factors and levels of design

<table>
<thead>
<tr>
<th>No</th>
<th>Factors code</th>
<th>Response Surfaces and Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>X₁=Adsorbent Dosage (g/L)</td>
<td>-α  -1  0  1  +α</td>
</tr>
<tr>
<td>2</td>
<td>X₂=Contact Time(min)</td>
<td>20  40  60  80  100</td>
</tr>
<tr>
<td>3</td>
<td>X₃=Temperature(°C)</td>
<td>30  60  90  120  150</td>
</tr>
<tr>
<td>4</td>
<td>X₄=Dilution Ratio</td>
<td>0,2  0,4  0,6  0,8  1</td>
</tr>
</tbody>
</table>

The experiments were carried out in the polyethylene bottles containing 100 mL of wastewater. The total hardness and calcium hardness amounts were measured using the
standard methods of 5340-C EDTA and 3500-Ca B codes. The percent of removal efficiency and the adsorption capacity are calculated according to the following equations.

\[
\% \text{Removal Efficiency} = \frac{C_0 - C}{C_0} \quad \text{Eq.1}
\]

\[
q(mg/g) = \frac{(C_0 - C) + V}{W} \quad \text{Eq.2}
\]

Here, the \(C_0\) and \(C\) are the hardness concentrations of wastewater (mg/lt), \(V\) is the volume of wastewater (lt) and \(W\) is the mass of the clinoptilolite sample (g).

3. Results
In this research, central composite design (CCD) of RSM was applied to evaluate the total hardness and calcium hardness removal efficiency from wastewater. The complete quadratic design model was composed of 25 experimental runs with 6 replicates at the central point. The experiments were carried out for the experimental conditions given in Table 3. The experimental results obtained for the raw and modified samples were also included in Table 3.

Table 3. Central Composite Design (CCD) for the study of four experimental variables

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Variables (coded)</th>
<th>Raw Clinoptilolite (%Removal Efficiency)</th>
<th>Clinoptilolite modified by HCl (%Removal Efficiency)</th>
<th>Clinoptilolite modified by NaOH (%Removal Efficiency)</th>
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<tbody>
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<td>25</td>
<td>0.6</td>
</tr>
<tr>
<td>31</td>
<td>60</td>
<td>90</td>
<td>25</td>
<td>0.6</td>
</tr>
</tbody>
</table>

The equations and regression values (R^2) obtained by RSM analyses of the experimental results are shown in Table 4. As seen Table 4, the high R^2 values, above 0.9 indicate the goodness of fit for the model.
Table 4. RSM based models and their accuracy values

<table>
<thead>
<tr>
<th>Responses</th>
<th>Final equation in terms of factors</th>
<th>R²</th>
<th>R²adj</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw clinoptilite</td>
<td>% Total Hardness Removal = -68,8 + 0,621 X₁ + 0,442 X₂ + 4,131 X₃ + 1,8 X₄ - 0,00384 X₁ X₃ - 0,00151 X₁ X₂ - 0,0804 X₁ X₄ + 0,00187 X₂ X₄ + 0,00038 X₁ X₄ + 0,00578 X₃ X₄ + 0,0069 X₂ X₄ + 0,445 X₃ X₄</td>
<td>0,9065</td>
<td>0,8247</td>
</tr>
<tr>
<td>Calcium Hardness</td>
<td>% Removal Efficiency</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clinoptilite modified by HCl</td>
<td>% Calcium Hardness Removal = -36,7 + 0,394 X₁ + 0,019 X₂ + 2,329 X₃ - 3,7 X₄ - 0,003910 X₁ X₂ - 0,001738 X₁ X₃ - 0,0771 X₁ X₄ - 13,57 X₂ X₄ - 0,000667 X₂ X₄ - 0,000818 X₁ X₄ + 0,0825 X₁ X₄ + 0,00040 X₁ X₁ + 0,1710 X₁ X₄ + 0,557 X₂ X₄</td>
<td>0,9561</td>
<td>0,9177</td>
</tr>
<tr>
<td>Calcium Hardness</td>
<td>% Removal Efficiency</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clinoptilite modified by NaOH</td>
<td>% Calcium Hardness Removal = 9,9 - 0,592 X₁ + 0,048 X₂ + 3,039 X₃ - 45,2 X₄ + 0,007337 X₁ X₁ - 0,000642 X₂ X₃ - 0,0201 X₁ X₄ + 0,001448 X₁ X₄ - 0,01919 X₁ X₄ + 0,00271 X₁ X₄ + 0,255 X₁ X₄ + 0,434 X₁ X₄</td>
<td>0,9830</td>
<td>0,9682</td>
</tr>
</tbody>
</table>

Using the model, the optimum conditions and effective parameters for removal of the total hardness and calcium hardness from the wastewater were determined. The validation experiments were carried out in the optimum conditions determined by RSM and the results consistent with the model were obtained. The optimum conditions and the comparison of the model outputs and experimental values at the optimum conditions are given in Table 5. As a result, the clinoptilolite modified by NaOH is the most convenient adsorbent and provides above %99 removal efficiency for total hardness and calcium hardness. In case of the use of clinoptilolite modified by NaOH, the total hardness adsorption capacity and calcium hardness adsorption capacity at the optimum conditions were obtained as 12,30 mg/g and 5,92 mg/g, respectively.

Table 5. The optimum conditions and experimental results
The contour graphs obtained by RSM show the effects of each two factors on removal efficiencies and adsorption capacities. The contour graphs of the experiments carried out with the clinoptilolite modified by NaOH are illustrated in the Fig.1, Fig. 2, Fig.3 and Fig.4.
Fig. 1. Contour plots of Total Hardness Removal

Efficiencies when using clinoptilolite modified by NaOH

Fig. 2. Contour plots of Total Hardness Adsorption Capacity (q)

Fig. 3. Contour plots of % Calcium Hardness Removal

Efficiencies when using clinoptilolite modified by NaOH

Fig. 4. Contour plots of Calcium Hardness Adsorption capacity (q)

References


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The Pyrolysis Bioproduct Characterization and Thermogravimetric Analysis of Waste Corn

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Keywords: Bio-products, pyrolysis, waste corn.

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

1. Introduction
Corn waste whose main chemical components contain abundant cellulose, hemicellulose and lignin is one of the by-products of grain crops (Li et al., 2016). So far the utilization of waste corn is not high, except for a limited comprehensive utilization as feed, fertilizer, industrial raw materials, fuel, and so forth (Xi et al., 2016).

The pyrolysis process offers an alternative way to convert to useful products. Pyrolysis is a thermal decomposition of organic substances under oxygen-absence circumstances into various phases: liquid products (condensable vapors at cooling temperature); carbon-rich solid residues (bio-char); gaseous products (syngas which were not condensable gases) (Bridgwater, 2012; Butler et al., 2011). The liquid product, namely bio-oil, which is a complex mixture of oxygenated hydrocarbons and water, holds the potential to become an alternative for transportation fuels and a source of synthetic chemical feedstock (Pootakham and Kumar, 2010).

Fast pyrolysis has been applied for many biomass types such as wood residues (Abnisa et al., 2013; Ki et al., 2013), and agricultural residues (Asadullah et al., 2013; Islam et al., 2010; Ji-lu, 2007) mainly for producing bio-oils. The yield of bio-oil shows large varieties from 33 wt.% to 65 wt.% depending on temperature and feedstock. Temperature was plotted to be the most decisive factor on bio-oil yields and lignin–cellulose content of feedstock affects the composition of bio-oil and its properties. However, catalysts were used in these studies.

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

2. Materials and Methods

2.1. Thermogravimetric study and pyrolysis of corn wastes

The decomposition behavior of corn waste samples was studied by the thermogravimetric simultaneous thermal analyzer (Mettler Toledo TGA/DSC1), whose temperature precision is ± 0.5 °C and microbalance sensitivity is less than ± 0.1 µg. The heating rate of 20 and 50 °C/min were carried out in this study.

Another pyrolysis experiment was carried out in a lab scale fixed bed reactor at heating rates of 3°C/min and 5°C/min. The properties of corn wastes were given in Table 1.

<table>
<thead>
<tr>
<th>Table 1. Properties of corn wastes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash Content (%)</td>
</tr>
<tr>
<td>---------------------------</td>
</tr>
<tr>
<td>0.62</td>
</tr>
</tbody>
</table>
2.2. Characterization of pyrolysis products

The collected bio-char and bio-liquid products were analysed. The specific surface area of bio-chars were determined using a Micromeritics TriStar II PLUS BET (Brunauer-Emmett-Teller) analyzer. The calorific values of bio-char and bio-liquid products were measured by calorimeter bomb. The bio-liquid fraction were analysed by using a gas chromatography-mass spectrometry (GC-MS).

2.3. Kinetic Models

In this work, the Ozawa-Flynn-Wall (OFW) method and the Kissinger-Akahira-Sunose (KAS) method were used to calculate the apparent activation energy with two different heating rates, as expressed in following Eqs. (1) and (2) (Fang et al., 2018; Leroy et al., 2010), respectively:

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

\[
\ln\left(\frac{\beta}{T^2}\right) = \ln\left[\frac{AE}{RG(\alpha)}\right] - \frac{E}{RT} \quad \text{Eq.2}
\]

where \(\alpha\) is the conversion degree, \(T\) is the reaction temperature, \(E\) is the activation energy, \(A\) is the pre-exponential factor, \(R\) is the universal gas constant, \(\beta\) is the heating rate (defined as \(dT/dt\)) and \(G(\alpha)\) is the temperature-independent function of reaction model. OFW method and KAS method are both non-isothermal and model-free methods. Without the introduction of the kinetic model function, thus they eliminate potential error brought by the false assumption of reaction mechanism and obtain more reliable activation energy.

3. Results

3.1. Thermogravimetric analysis of corn wastes

The mass loss (TG) and derivative mass loss (DTG) curves of corn wastes at the heating rate of 20°C/min and 50°C/min under CO2 atmosphere were shown in Figure 1. The crossover point between two stages is defined as the midpoint of the line between two tangent lines. For 20°C/min and 50°C/min heating rates, the final temperature of pyrolysis is acquired when the biomass loss is 94.4% and 85.8% of the total weight loss, respectively.
Figure 1. TG curves at the heating rate of (a) 20 °C/min and (b) 50°C/min of corn wastes

3.2. Kinetic Analysis

By using Eqs. (1) and (2), Figure 2 elucidated the apparent activation energy (E) fluctuation of corn waste under different conversion degree α. E value calculated by OFW method were slightly higher than E value calculated by KAS method, but the fluctuation trend of both methods was the same. The similar diversity between OFW and KAS method was found elsewhere, it probably derived from the different essences in formula. OFW method applied Doyle’s approximation of \( p(x) = -2.315 + 0.457x \), while KAS method used approximation of \( p(x) = x - 2e^{-x} \). 50°C/min heating rate resulted in milder mass loss rate and higher averaged apparent activation energy (E) value, this heating rate showed the highest E (429 kJ/mol (KAS) and 457 kJ/mol (OWF)).
In Table 2, thermokinetic parameters were given. Difference between the values of activation energies and enthalpies (ΔH) reflects the feasibility of the reaction. Lower the difference between E and ΔH, more preferred the product formation would be. A difference of ∼5 kJ mol$^{-1}$ was observed between the E and ΔH values which reflect that product formation would be easier to achieve.

As seen from Table 2, activation energy for corn waste pyrolysis was compatible with previously reported values for various agriculture wastes. Although pea waste showed a potential to be a suitable candidate for pyrolysis process, its low production rate can hinder its industrial scale application. Thus, valorization of corn waste together with some other type of agriculture wastes or its blend with coal can be considered for sustainability.

When conversion values increased, ΔG and ΔS values were increased. Gibbs free energy (ΔG) reveals the amount of energy that available from that corn waste upon combustion. Here, the ΔG values were shown to be ranging from 115.2 to 139.9 that lower when compared with the ΔG values of the para grass (169–171), waste rice straw (164.59 kJ mol$^{-1}$), rice bran (167.17 kJ mol$^{-1}$) and pepper waste (139.4 kJ mol$^{-1}$) (Chen et al., 2016).

<table>
<thead>
<tr>
<th>α</th>
<th>E (kJ/mol)</th>
<th>T (°K)</th>
<th>ΔH(kJ/mol)</th>
<th>ΔG (kJ/mol)</th>
<th>ΔS (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>192</td>
<td>504</td>
<td>124</td>
<td>115.2</td>
<td>17.8</td>
</tr>
<tr>
<td>0.2</td>
<td>231</td>
<td>530</td>
<td>155</td>
<td>134.5</td>
<td>39.6</td>
</tr>
<tr>
<td>0.3</td>
<td>272</td>
<td>546</td>
<td>167</td>
<td>137.7</td>
<td>54.9</td>
</tr>
<tr>
<td>0.4</td>
<td>298</td>
<td>584</td>
<td>157</td>
<td>139.9</td>
<td>30.8</td>
</tr>
<tr>
<td>0.5</td>
<td>313</td>
<td>598</td>
<td>164</td>
<td>135.7</td>
<td>48.4</td>
</tr>
<tr>
<td>0.6</td>
<td>387</td>
<td>614</td>
<td>197</td>
<td>137.2</td>
<td>97.7</td>
</tr>
<tr>
<td>0.7</td>
<td>429</td>
<td>630</td>
<td>281</td>
<td>137.9</td>
<td>228.5</td>
</tr>
</tbody>
</table>

3.3. Pyrolysis behavior and product yields

Product yields of corn wastes pyrolysis process are shown in Figure 3. According to this figure, gas production was between 18%–28% between 300°C and 700°C. As temperature increases, organic structure of corn waste is degraded and new gas products having high molecular weight are created. The amount of bio-gas product was 66% for 3°C/ min at 300°C which was the lowest pyrolysis temperature. However this value was found to be as 70% at the higher temperature (700°C). Waste corn began to get degraded into bio-gas products and therefore the amount of bio-oil product increased. At 5°C/ min, bio-oil yields

![Figure 2. The relationship between α and E](image-url)
were higher than 3°C/min for all pyrolysis temperature. 8.3% of HDPE char remained at pyrolysis temperature of 300°C for 5°C/min. As temperature was increased from 300°C to 700°C, bio-char turned into bio-gas products. At 3°C/min and 5°C/min, 7.6% and 7.7% char remained at the system, respectively. As result, similar bio-product yields were obtained for 3°C/min and 5°C/min heating rates.

**Figure 3.** Bio-product yields

### 3.4. Characterization of pyrolysis bio-products
Composition of bio-liquid were given in Table 3. According to the GC-MS results, when the heating rate and the pyrolysis temperature were increased while the benzene, toluene, o-xylene, m-xylene, dimethylbenzene, trimethylbenzenes, indane and indene compounds were observed in all the liquid products, it was observed that the compounds of the alkane and alken group in the liquid product were changed into other compounds. When the pyrolysis temperature and heating rates increased, complex compounds converted to low molecular weight compounds like benzene and methyl groups.

**Table 3.** Composition of bio-liquid

<table>
<thead>
<tr>
<th>300°C-3°C/min</th>
<th>300°C-5°C/min</th>
<th>700°C-3°C/min</th>
<th>700°C-5°C/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>Benzene</td>
<td>Benzene</td>
<td>Benzene</td>
</tr>
<tr>
<td>Toluene</td>
<td>Toluene</td>
<td>Toluene</td>
<td>Toluene</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>o-Xylene</td>
<td>o-Xylene</td>
<td>o-Xylene</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>m-Xylene</td>
<td>m-Xylene</td>
<td>m-Xylene</td>
</tr>
<tr>
<td>Dimethylbenzene</td>
<td>Dimethylbenzene</td>
<td>Dimethylbenzene</td>
<td>Dimethylbenzene</td>
</tr>
<tr>
<td>Trimethylbenzenes</td>
<td>Trimethylbenzenes</td>
<td>Trimethylbenzenes</td>
<td>Trimethylbenzenes</td>
</tr>
<tr>
<td>Indane</td>
<td>Indane</td>
<td>Indane</td>
<td>Indane</td>
</tr>
<tr>
<td>Indene</td>
<td>Dimethylnaphthalene</td>
<td>Indene</td>
<td>Dimethylnaphthalene</td>
</tr>
<tr>
<td>Methylindenes</td>
<td>Acenaphthylene</td>
<td>Methylindenes</td>
<td>Acenaphthylene</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>Acenaphthene</td>
<td>Naphthalene</td>
<td>Acenaphthene</td>
</tr>
<tr>
<td>Methylnaphthalenes</td>
<td>Ethynaphthalene</td>
<td>Methylnaphthalenes</td>
<td>Ethynaphthalene</td>
</tr>
<tr>
<td>Ethynaphthalene</td>
<td>Dimethylnaphthalene</td>
<td>Ethynaphthalene</td>
<td>Dimethylnaphthalene</td>
</tr>
<tr>
<td>Dimethylnaphthalene</td>
<td>Trimethylnaphthalenes</td>
<td>Dimethylnaphthalene</td>
<td>Trimethylnaphthalenes</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>Fluorene</td>
<td>Acenaphthene</td>
<td>Acenaphthene</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>Tetramethylnaphthalene</td>
<td>Acenaphthene</td>
<td>Tetramethylnaphthalene</td>
</tr>
</tbody>
</table>
Analysis results of bio-char were given in Table 4. The pyrolysis temperature have little influence on bio-char properties, as the results do not show great variety. Carbon, as the main element in all of the produced bio-chars (91–95 wt.%), is present in significantly greater amounts from other elements. In comparison to raw waste corn, the O content (3.2–3.8 wt.%) and H content (0.87–1.25 wt.%) decrease in all the bio-char samples due to dehydration and decarbonylation/decarboxylation reactions. The HHV of bio-char samples is highly dependent on hydrogen and carbon contents of the samples. Generally, when C and H content increased HHV and LHV values increased. The bio-char samples have HHV values (47.2–51.57 MJ/kg) comparable to those of some coals and are therefore acceptable for use as a renewable solid fuel. According to BET analysis results, heating rate and pyrolysis temperature increased, BET and Vpore values increased.

Table 4. Properties of bio-char

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

4. Conclusion

In this study, thermogravimetric properties of corn waste were investigated by TGA analysis. However, this waste pyrolysed in laboratory scale system under different pyrolysis conditions. According to study results, the final temperature of pyrolysis is acquired when the biomass loss is 94.4% and %85.8 of the total weight loss for 20°C/min ve 50°C/min heating rates. 50°C/ heating rate showed the highest E (429 kJ/mol (KAS) and 457 kJ/mol (OWF)). When conversion values increased, ΔG and ΔS values were increased. In pyrolysis process, bio-gas production was between 18%-28% between 300°C and 700°C. At 5°C/ min, bio-oil yields were higher than 3°C/ min for all pyrolysis temperature. 8.3% of HDPE char remained at pyrolysis temperature of 300°C for 5°C/ min. As temperature was increased from 300°C to 700°C, bio-char turned into bio-gas products. The pyrolysis temperature have little influence on bio-char properties, as the results do not show great variety.

References


Use of Polymer-Zeolite Based Composite Adsorbent for the Removal of Mixed Heavy Metals

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Keywords: Adsorption, Alginate, Cadmium, Clinoptilolite, Copper, Lead

Abstract

Due to rapid industrial development, particularly water quality is decreased by various pollutants. Heavy metals are one of them leading toxicity. Therefore, treatment of these metals is required to protect the nature. Adsorption, is an alternative method, has been still under investigation giving chance to regain of discharged heavy metals. Lots of adsorbents are utilized for this purpose. In this study, alginites (A), natural biopolymers from brown algae, were applied together with clinoptilolite (C) in bead forms. A-C beads were used to remove heavy metals from synthetic wastewaters in batch reactors. Results showed that A-C beads were efficient for the treatment of mixed metal solutions. Adsorption of Pb\(^{2+}\) was favorable compared to Cu\(^{2+}\) and Cd\(^{2+}\). Furthermore, evaluation of equilibrium kinetics was compatible with pseudo second order model.

1. Introduction

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

There are lots of methods, such as chemical precipitation, ion exchange, ultra filtration and reverse osmosis, used for heavy metal removal from wastewaters. However, adsorption can be a good alternative if the adsorbent is natural, easy to find and economic (Fu and Wang, 2011). Recently, studies have focused on natural adsorbents. Thus, alginites, which are currently harvested from brown algae, are getting attention. This biopolymer can capture metals particularly by carboxyl groups in their structure. On the other hand, since alginate like cheap adsorbents’ treatment capacities are not enough to use them in real applications, researchers continue to seek more efficient adsorbents (Bakr et. al., 2015, Kragovic et. al., 2018, Lim et. al., 2009, Roh et. al., 2015, Shawky, 2011). Likewise, the main aim of this study is to increase heavy metal adsorption capacity of alginate. For this purpose, clinoptilolite, which is a zeolite having abundant source in Turkey, was selected. Then, A-C beads were investigated for the removal of Cu\(^{2+}\), Cd\(^{2+}\), Pb\(^{2+}\) heavy metals from synthetic wastewaters by using batch reactors.

2. Materials and Methods

Effects of clinoptilolite size, A/C ratio, pH, heavy metal concentrations and adsorption kinetics were investigated in the study. Only the results obtained from the evaluation of adsorption kinetics are presented here.
Clinoptilolite (10 g) was first sieved into the size lower than 100 µm, then conditioned by using NaCl (1 M) during 24 hours at 200 rpm and finally dried. For A-C beads, alginate (2%) was combined with clinoptilolite, from Manisa-Gördes, at a ratio of 1g A/1g C. After that the beads were formed by dropping into CaCl2 solution (50 mM). Finally, A-C beads were incubated overnight, washed, filtered and dried.

Experiments for comparison of adsorption capacities of alginate, clinoptilolite and A-C beads were performed by using 100 mg adsorbents. They were subjected to a mixture of Cu2+, Cd2+, Pb2+ as 100 mg/L solution of each metal at pH 4 and 30 °C for 24 hours at 150 rpm. Similarly, adsorption kinetics was determined using 100 mg A-C beads at the same conditions by time dependent sampling during 48 hours. All were filtered, acidified and cooled until metal analysis.

The data evaluation for kinetics of adsorption was performed by using common methods such as pseudo first and second order models. The equations related to these models can be summarized as following:

According pseudo first order model;

\[ \frac{dq_t}{dt} = k_1 \times (q_e - q_t) \]

\[ \log (q_e - q_t) = \log (q_e) - \frac{k_1}{2.303} \times t \]

Where k1 is first order rate constant (1/min), qe and qt are the amount of matter adsorbed at equilibrium and time t (mg/g). When the graph log (qe – qt) versus t is drawn, slope and the intercept can be used to calculate qe and k1 values (Ho 2002).

Pseudo second order model;

\[ \frac{dq_t}{dt} = k_2 \times (q_e - q_t) \]

\[ \frac{1}{q_t} = \frac{1}{k_2 \times q_e^2} + \frac{1}{q_e} \times t \]

Where k2 is second order rate constant (g/mg.min), qe and qt are the amount of matter adsorbed at equilibrium and time t (mg/g). When the graph t/qt versus t is drawn, slope and the intercept can be used to calculate qe and k2 values (Duman 2012).

3. Results

Alginates are combined with clinoptilolite to form composite beads for heavy metal removal in the current study. Figure 1 shows the results obtained from adsorption of heavy metals by alginate and clinoptilolite alone and also A-C beads. Regardless of the adsorbent, one can say that Pb2+ is the most adsorbed heavy metal with the highest removal efficiency of 92 % by A-C beads after 24 hours. This value corresponds to 45 mg Pb2+/g A-C beads. In another study (Akgül, 2009), adsorption capacities for Pb2+ were found as 19.62 and 122.4 mg Pb2+/g zeolite at initial Pb2+ concentrations of 50 and 400 mg/L, respectively. On the other hand, Cu2+ removal efficiencies followed Pb2+ reduction while all adsorbents had the lowest affinity to Cd2+. Similarly, alginate was found a good adsorbent for lead and copper (Moral et. al., 2012). Both clinoptilolite and alginate heavy metal removal efficiencies were lower compared to A-C beads. For example, about 100 mg/L of Pb2+ was decreased around 8 mg/L by using A-C beads while it was 23 mg/L and 50 mg/L by alginate and clinoptilolite alone, respectively. Consequently, heavy metal adsorption capacity of alginate was improved by proposed A-C bead combination.
Adsorption of mixed metal solution by A-C beads was followed during 48 hours and the findings are summarized in Figure 2. As it is seen from the figure, adsorption of heavy metals is observed to be faster during early times of the experiments. Equilibrium times for Cu$^{2+}$ and Cd$^{2+}$ were found as 24 hours while it was 8 hours for Pb$^{2+}$. Longer equilibrium times might be related with porous structure of the adsorbent. Similar results were obtained by Türe et al (2017). Also, it seems the A-C beads prefer to take Pb$^{2+}$ more efficiently compared to the other metals since almost all of Pb$^{2+}$ can be removed from the solution. This is probably explained by the difference in the affinity of metals towards the composite adsorbent. Furthermore, the maximum removal efficiencies were calculated for Cu$^{2+}$ and Cd$^{2+}$ as 82 and 74 %, respectively. Adsorption capacity was also higher in the case of Pb$^{2+}$ being around 48 mg Pb$^{2+}$/g A-C beads.

Figure 1. Heavy metal removal by (a) alginate, (b) clinoptilolite, and (c) A-C beads.
The data obtained from adsorption of Cu$^{2+}$, Cd$^{2+}$ and Pb$^{2+}$ by A-C beads were evaluated to elucidate kinetics of adsorption. Common models, pseudo first and second order models, as summarized in materials and methods section are utilized for this purpose. The results are presented in Figure 3. The higher $R^2$ values for best fitted lines claim the higher correlation for the related models. Thus, as it is seen from the figure, one can say that adsorption kinetics are compatible with pseudo-second order model. Adsorption rate constants for the metals are changing in the range of 0.02 – 0.047 mg/g.min. Likewise, Sigdel et al (2017) also showed that adsorption of Cd$^{2+}$ can be expressed by pseudo second order model.

**Figure 2.** Kinetics of heavy metal removal by A-C beads.

**Figure 3.** Heavy metal adsorption kinetics by A-C beads (a) Cu$^{2+}$; (b) Cd$^{2+}$; (c) Pb$^{2+}$ of pseudo first order (left) and pseudo second order (right).

**References**


Epoxy Composites with Washed PS Wastes Pyrolysis Char Additives

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Keywords: Char, composite, pyrolysis, PS waste

Abstract

This study presents pyrolysis of PS waste (washed) and preparation of epoxy composite with pyrolysis char. In the scope of the study, PS wastes were pyrolysed in fixed-bed pyrolysis reactor at different temperatures and epoxy composite materials prepared with PS char were analyzed for mechanical, electrical and thermogravimetric properties.

1. Introduction

The amount of plastic waste generated every year is estimated to be increasing at a rate of 3.9% per year (Plastic Europe, 2015). This, combined with the existing amount of municipal solid waste, make the management of plastic waste an ever-increasing problem. Additionally, owing to many countries' increasing desire for energy independence, there is a growing interest in alternatives to fossil fuels with waste derived feedstocks, like waste biomass and plastic waste, receiving most of the attention mainly due to their abundance and environmental benefits.

In 2013, 299 million tons of plastic waste was generated globally, with the European Union alone generating more than 25.2 million tons of post-consumer plastic waste each year (Plastic Europe, 2015). Of this, around 26% is recycled, 36% is recovered by energy recovery processes, such as incineration, and the remainder is landfilled. Incinerating...
plastics can cause several environmental issues, such as dioxins formation, fly ash, production of sulphur and nitrogen oxides, and other toxins (Gordon et al., 2002, Qinghai et al., 2010)

Polystyrene (PS) is the most employed aromatic thermoplastic polymer. PS finds a wide range of application from food contact packaging to thermal insulator in buildings. In 2011 the European production of PS was $3.5 \times 10^9$ kg, and its disposal is an environmental and social problem which is ceaselessly addressed from academic and industrial researchers (Plastic Europe, 2012).

Pyrolysis is a suitable process for oil based material, where the plastic waste is heated in absence of oxygen to break the long chain hydrocarbons into intermediate and small chain hydrocarbons. Pyrolysis can be classified into slow pyrolysis, fast pyrolysis and flash pyrolysis depending upon their heating rate, residence time and temperature (Prathiba et al., 2018).

Thermal degradation involves cracking of large chain hydrocarbons into small chain hydrocarbons at high temperatures (300-600°C). The pyrolysis process is completed in three major steps: initiation, propagation and termination. The products produced from pyrolysis differ in yield and composition due to various parameters which includes type of feedstock, reactor system, residence time of gas, heating rate, contact time, temperature, pressure ranges, effect of catalysts (if any present) and presence of hydrogen gas or hydrogen giving compounds (Williams et al., 2007; Shah et al., 2005; Acma et al., 2006; Kaminsky et al., 2007). The pyrolysis process is further divided on the basis of these parameters into slow and fast pyrolysis.

The pyrolysis process converts organic materials including plastic waste into energy (liquid oil and gas) and value-added product (char) (Bartoli et al., 2015; Rathore et al., 2016; Demirbas et al., 2016b).

Char such as activated carbon has great potential for the production of better quality pyrolytic products. Hence, this field needs to be further studied. The char residue is present on the feedstock, when the feedstock is pyrolysed, the behavior of the char produced is determined by following characteristics: (a) the disorganized and porous structures; (Gilbert et al., 2009, Liu et al., 2014)(b) the presence of O-containing groups on the char surface; (Wang et al., 2014; Ducousso et al., 2015) (c) the structure of the carbonaceous matrix; (Keown et al., 2008; Fu et al., 2009) (d) active sites formed by the alkaline (Na, K) and alkaline earth (Mg, Ca) species distributed in the char matrix (Klinghoffer et al., 2015).

Epoxy resins are thermosetting polymers. These resins are produced as glycidyl (glycidyl ester) and non-glycidyl (cyclo aliphatic). Glycidyl epoxy resins is produced using Bisphenol-A and is produced in a reaction with epichlorohydrin (Johnson, 2017).

Generally, epoxy composite materials are obtained from epoxy resins. The epoxy resins are produced from matrix and particles as filler material. These particles are obtained from talc, calcium carbonate or synthetic fillers such as carbon black. The important environmental impacts of the epoxy resins are consumption of petroleum sources. Among the ingredients of epoxy resins, epoxide groups is the largest contributor to greenhouse effect by pollutant emissions. The other important impact is the significant amounts of energy requirement of epoxy resin production. Each ton of epoxy resin production consumes 145 kW-h electricity, on average. Epoxy resin production requires a lot of energy and material usage.
Raw materials of epoxy resins can be obtained from natural sources. As a result, environment and economy can be protected.

In this article presents pyrolysis of real PS waste (washed) and preparation of epoxy composite from pyrolysis char. In scope of study, PS waste were pyrolysed in fixed-bed pyrolysis reactor at different temperatures without catalyst and epoxy composite materials obtained from PS char were analyzed for determination of mechanical, electrical and thermogravimetric properties.

2. Materials and Methods

2.1. Characterization of Char

Waste PS plastics crushed in plastic crusher were pyrolysed at 300°C, 500°C and 700°C for 5°C/min heating rate. Solid product (char), oil product and gas product were obtained from pyrolysis system. Char product remained as solid product in the reactor.

Scanning electron microscopy (SEM) was used to scan the surface morphology of char with a Zeiss Evo LS 10 instrument. The functional group composition of char products were determined by Fourier transform infrared (FTIR).

2.2. Preparation of Epoxy Composites

Chars obtained from pyrolysis reactor have lumpy structure. Because char samples were ground before being mixed with epoxy resin (ER).

Doses of 10, 30 and 50 wt% were selected. Accurately weighed char was added to the ER stirred for 3 hours at 2000 rpm by mechanical mixer. 30 wt% epoxy hardener and 1 wt% epoxy accelerator were added into the mixture. The final mixture was degassed for 60 minute at 40°C and this mixture transferred into the mold. ASTM D 638 standards were used for preparation of composite samples (ASTM-D638, 2002).

The curing process was applied in an oven at 40°C for 1 day and then post cured at 60–120°C within two day. Three composite sample were prepared for for physical properties tests and electrical properties test.

Surface morphology of the prepared epoxy composites were scan by SEM. were performed TGA analyzer were used for thermogravimetric analyses of composite materials. TGA analysis was conducted under flowing nitrogen atmosphere at atmospheric pressure. 10 mg of composite was heated up to 900°C in a porcelain crucible. The sample weight loss and rate of weight loss were recorded continuously as functions of time or temperature.

Electrical properties of the epoxy composites were determined with an electrometer. Hardness tester (Shore Durometer TH 210) was used for measuring hardness of the composites. Stretch and pressing equipment (TST-Mares/TS-mxe) were used for the stretch resistance properties.

According to ASTM D-570, the effect of water absorption on epoxy composites were investigated. Weighted composite samples were waited in distilled water at room temperature for 12 hours. The samples were weighted by precision weighing equipment.
3. Results

3.1. Properties of char samples

SEM images showing topographic structure of char samples are shown in Figure 1. All char samples have spherical structure. As the temperature increases, depolymerization of waste PS increased. The particular distribution of 700°C char is more homogeneous compared to other samples. With the increasing of temperature, the surface of char product becomes irregularity due to the shrinkage of spherical structure which is caused by devolatilization. This results can be seen from SEM images of chars where best depolymerization were seen in 700°C char as compared to 300°C and 500°C chars. For all char samples, small particles with spherical shape are observed. Some particles come from contaminants attached on waste PS plastics. Others may be due to pyrolytic carbon deposits resulting from hydrocarbons cracking.

![Figure 1. SEM images of char samples](image)

Figure 2 is present the FTIR spectra of the pyrolysis char obtained from the pyrolysis of PS wastes. In the pyrolysis char obtained at 300°C, aliphatic C-H peaking at 3000-2000 cm\(^{-1}\) wave number, aromatic C-H at 1000-800 cm\(^{-1}\) and aromatic C-C groups at 1700-1450 cm\(^{-1}\) wave number were determined. As the temperature increased, the aliphatic C-H functional groups groups were decomposed and these groups showed no peak at 600°C and 700°C. At these temperatures, aliphatic C-H and aromatic C-C groups remained.
The elongation at break (%), tensile strength and hardness values of composites obtained from PS char were determined. The results were given in Table 1. As the pyrolysis temperature increased up to 500 °C, the tensile strength, elongation at break and Young's modulus values of PS composites increased. However, the tensile strength and Young's modulus of PS composites were higher than raw ER for all pyrolysis temperatures. According to the results obtained from the hardness measurement, there was an increase in the superficial hardness of the composites, and for the composites of the same dose, the hardness values were increased as the pyrolysis temperature increased.

**Table 1.** The effect of pyrolysis temperature and char doses on mechanical properties of composite samples

<table>
<thead>
<tr>
<th>Pyrolysis Temperature (°C) and Doses (%)</th>
<th>Elongation at Break (%)</th>
<th>Tensile Strength (MPa)</th>
<th>E-modulus (GPa)</th>
<th>Hardness (Shore D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw ER</td>
<td>0.721</td>
<td>86</td>
<td>6.2</td>
<td>80</td>
</tr>
<tr>
<td>Composites</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300°C (%10)</td>
<td>0.990</td>
<td>106</td>
<td>7.5</td>
<td>85</td>
</tr>
<tr>
<td>300°C (%30)</td>
<td>1.010</td>
<td>123</td>
<td>8.8</td>
<td>85</td>
</tr>
<tr>
<td>300°C (%50)</td>
<td>0.600</td>
<td>87</td>
<td>6.1</td>
<td>86</td>
</tr>
<tr>
<td>500°C (%10)</td>
<td>1.326</td>
<td>147</td>
<td>6.6</td>
<td>86</td>
</tr>
<tr>
<td>500°C (%30)</td>
<td>1.233</td>
<td>141</td>
<td>11</td>
<td>86</td>
</tr>
<tr>
<td>500°C (%50)</td>
<td>0.989</td>
<td>140</td>
<td>9.2</td>
<td>86.5</td>
</tr>
<tr>
<td>700°C (%10)</td>
<td>1.303</td>
<td>132</td>
<td>8.8</td>
<td>87</td>
</tr>
<tr>
<td>700°C (%30)</td>
<td>0.974</td>
<td>130</td>
<td>9.8</td>
<td>86</td>
</tr>
<tr>
<td>700°C (%50)</td>
<td>0.766</td>
<td>105</td>
<td>8.3</td>
<td>87</td>
</tr>
</tbody>
</table>

The electrical conductivity measurement results of PS composites were given in Table 2. As the pyrolysis temperature increased, there was an increase in the electrical conductivity values of the composites.
### Table 2. Electrical conductivities of composite samples

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>%10</th>
<th>%30</th>
<th>%50</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>$5.04 \times 10^{-8}$</td>
<td>$1.43 \times 10^{-7}$</td>
<td>$1.90 \times 10^{-7}$</td>
</tr>
<tr>
<td>500</td>
<td>$7.91 \times 10^{-7}$</td>
<td>$1.84 \times 10^{-6}$</td>
<td>$5.99 \times 10^{-5}$</td>
</tr>
<tr>
<td>700</td>
<td>$8.64 \times 10^{-6}$</td>
<td>$6.58 \times 10^{-5}$</td>
<td>$1.08 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

In Figure 3, water absorption behavior of composite samples were given graphically. For all composite samples, as the char ratio were increased, the absorbed water amount were increased. Also the amount of water absorbed in the 700°C composite was less than the other samples. The decrease in water absorption of composite samples obtained from 700°C pyrolysis char compared to other composite samples is attributed to the formation of good interface bond between resin and chars reduces the tendency to absorbed water through capillary action.

![Figure 3. Water adsorption of composite samples, (a)300°C, (b)500°C and (c)700°C](image)

### 4. Conclusion

Epoxy composite material was produced by adding char that was the solid product of pyrolysis of washed PS plastic wastes between 300°C and 700°C. As the dose in composite material obtained by char sample obtained for all pyrolysis temperatures for PS was increased, electrical conductivity of the composites also increased. Composite materials produced at temperatures and all doses had semi-conductor structure. Epoxy composite material obtained by PS pyrolysis char obtained at 300 °C showed the most ideal behavior in terms of breaking elongation and tensile strength. This study provided an alternative method for recovery of waste PS plastic wastes.

### Acknowledgement

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Utilization of Sulfonated Polystyrene in the Treatment of Waste PS Plastic Washing Wastewater

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Keywords: Coagulation-flocculation, PS, waste PS sulfonation

Abstract

PS (Polystyrene) waste washing wastewater contains high concentrations of turbidity, COD (Chemical Oxygen Demand), SS (Suspended Solids) and oil-grease that lead to an increase in the pollution load of wastewater treatment plant. In this study, a flocculant (FSPS) was synthesized from waste Polystyrene (PS) by sulfonation and it was used in coagulation-flocculation treatment of PS plastic washing wastewater. Turbidity, COD, SS and oil-grease analyses were performed at the supernatant. Effects of pH were studied at between pH 3-13. Alum and FeCl₃ were used as conventional coagulants (at 15-1000 mg/L dosages) in addition to flocculants the synthesized FSPS and polyelectrolyte (PEL) (between 5-50 mg/L dosage). At the pH 3 of the wastewater, 1000 mg/L Alum+20 mg/L FSPS resulted in 96% turbidity, 75% COD, 95% SS and 65% oil-grease removals, while for At the original pH of the wastewater (13±1) 1000 mg/L FeCl₃+5 mg/L FSPS, they were 88%, 71%, 93% and 83%, respectively. The produced FSPS resulted in higher and/or close performances with PEL.

1. Introduction

In developed countries, plastic consumption has grown remarkably over the past two or three decades (Mudgal et al., 2013). Industry is increasingly moving towards reusing and reprocessing plastics for economic and environmental reasons, with many companies developing technologies and strategies for recycling plastics (Nhamo et al., 2016). Environmental Protection Agency grouped waste material as hazardous and non-hazardous (URL1). Hazardous wastes, which may include chemicals, heavy metals, or substances created from byproducts of commercial manufacturing processes and disposed household products, are potentially harmful to both human health and environment (URL2). However, non-hazardous wastes, which may have the opportunities for reduction, reuse, and recycling, are not specifically hazardous (URL3).

The coagulation-flocculation is a process commonly used for the treatment of raw wastewater. During the flocculation process, the flocculation effects mainly depend on the choice of flocculants directly. A number of flocculants are commercially available, but some of them have been received attention for their negative environmental consequences and potential health impacts (Jin et al., 2013). For example, the use of inorganic salts, such as aluminum chloride or aluminum sulfate, is now disputed due to their potential contribution to Alzheimer's disease (Divakaran et al., 2001) and production of large scale of sludge (Renaut et al., 2009). Therefore, it is useful to find an efficient technique to recycle waste polystyrene with a more efficient method. A method was developed by 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, the treatability of contaminated PS washing processes wastewater by using synthesized sulfonated PS in coagulation/flocculation is investigated. The study was based on the sulfonation of waste polystyrene to produce a polymeric flocculant and its utilization for the removal of turbidity, COD, oil-grease and SS from wastewater. Its effectiveness in the treatment was also compared with conventional flocculant, polyelectrolyte (PEL). In this way, both recycling plastic waste and decreasing the urban wastewater treatment facility load will have been contributed.

2. Materials and Methods

2.1. Waste Plastic Washing

Washing of PSW which is crushed to 8 mm was performed in three steps. In the first step, waste PS was boiled in 42% of NaOH at 90°C for 10 minutes (Sandos et al, 2005). In the second and third steps, plastics obtained from this first step were boiled with tap water at 90°C for 10 minutes for rinsing. Waste plastic was left to dry. In the end of washing and two rinsing processes, plastic washing wastewater was obtained by combining these three effluents. Characterization of this PS washing wastewater is given in Table 1. COD, SS, oil-grease, pH and turbidity analyses were performed according to Standard Methods (APHA, 2005). Due to the contaminants on plastic waste, COD, SS and turbidity values are high. As washing process was performed with highly concentrated caustic solution, the pH and Na values are high.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>HDPE washing wastewater</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD₅ (mg/L)</td>
<td>1560±750</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>4140±790</td>
</tr>
<tr>
<td>SS (mg/L)</td>
<td>1710±160</td>
</tr>
<tr>
<td>Oil-Grease (mg/L)</td>
<td>4621±960</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>2840±480</td>
</tr>
<tr>
<td>pH</td>
<td>13±1</td>
</tr>
<tr>
<td>Pb (mg/L)</td>
<td>0,01±0,009</td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>16,78±1,4</td>
</tr>
<tr>
<td>Mn (mg/L)</td>
<td>0,17±0,08</td>
</tr>
<tr>
<td>Na (mg/L)</td>
<td>17550±17300</td>
</tr>
<tr>
<td>S (mg/L)</td>
<td>103,3±45</td>
</tr>
<tr>
<td>Mg (mg/L)</td>
<td>2,32±1</td>
</tr>
<tr>
<td>K (mg/L)</td>
<td>92,37±40</td>
</tr>
<tr>
<td>Ca (mg/L)</td>
<td>10,2±1</td>
</tr>
<tr>
<td>Cr (mg/L)</td>
<td>0,12±0,05</td>
</tr>
<tr>
<td>P (mg/L)</td>
<td>16,35±5</td>
</tr>
</tbody>
</table>

2.2. Sulfonated PS Flocculant (FSPS) Synthesis

Sulphonated PS flocculant was synthesized by the method of Vink (1981). Accordingly crushed waste was dissolved in cyclohexane. P₂O₅ was dissolved in H₂SO₄. The two solutions were mixed and kept at 40°C for an hour. The sub-phase was separated, distilled water was slowly added to the mixture of supernatant polymer. Powdery FSPS flocculant was obtained by making the mixture dried at 40°C for a day.
2.3 Treatment with coagulation-flocculation

Coagulation-flocculation studies were performed with Jar-test. Alum and FeCl₃ as coagulant agent and polyelectrolyte (PEL) and synthesized FSPS as flocculant agent were used. The coagulant doses of 15-1000 mg/L and the flocculant doses of 5-50 mg/L were selected. Coagulant agent was added into 250 mL wastewater sample and the following conditions were applied: rapid mixing in 125 rpm for 90 seconds for coagulation and a slow mixing in 25 rpm for 15 minutes for flocculation. After 1 hour sedimentation, analyses of turbidity and other parameters (COD, SS and oil-grease) were performed in the supernatant phase samples. Based upon findings, the most efficient coagulant dose was determined and experiments were performed in varied flocculant doses by fixing this value. After two most efficient flocculant doses were determined, the effects of pH were studied by changing the initial pH of the sample to 3, 5, 7 and 9.

3. Results

3.1 Effect of pH and Coagulants and Flocculants Dose on Treatment of Plastic Washing Wastewater

Change in turbidity with Alum and FeCl₃ doses for PS washing wastewater is given in Figure 1. FeCl₃ was more efficient than alum in turbidity removal (30-70%). The highest efficiency was achieved with 1000 mg/L for both Alum and FeCl₃ for PS washing wastewater. In the next steps, the coagulant dose was fixed at this value and five flocculant doses (5, 10, 20, 40 and 50 mg/L) were tested. The two most efficient flocculant doses were identified.

![Figure 1. Change of turbidity with Alum and FeCl₃ dose](image)

Changes in parameter values with flocculant dosage are indicated in Figure 2 for waste PS washing wastewater. Accordingly, Alum+20 mg/L and 40 mg/L FSPS, Alum+40 mg/L and 50 mg/L PEL, FeCl₃+5 mg/L and 10 mg/L FSPS and FeCl₃+5 mg/L and 10 mg/L PEL were determined as the two most efficient flocculant doses for each coagulant. Turbidity removal efficiencies were 51% for Alum+40 mg/L, 51% for Alum+50 mg/L PEL, 88% for FeCl₃+5 mg/L FSPS and 89% for FeCl₃+5 mg/L PEL. COD removal efficiencies were 69% for Alum+40 mg/L FSPS and 71% for FeCl₃+5 mg/L FSPS. SS removal efficiencies were 61%
for Alum+40 mg/L FSPS and 93% for FeCl₃+5 mg/L FSPS. Oil-Grease removal efficiencies were 65% for Alum+40 mg/L FSPS and 83% for FeCl₃+5 mg/L FSPS (Figure 2). FSPS flocculant with coagulant resulted in higher and/or similar efficiencies with PEL.

Figure 2. Turbidity, COD, SS and Oil-Grease change with FSPS and PEL dose for HDPE washing wastewater

1000 mg/L coagulant doses and the most efficient two selected flocculants were kept constant and the same treatments were repeated at initial pH values of 3, 5, 7 and 9 in the combination of Alum + FSPS and Alum + PEL (Figure 3). For pH 9, the turbidity removal efficiencies were observed for Alum+20 mg/L FSPS as 96% and for Alum+40 mg/L PEL as 98%. For the pH value of 7, the turbidity removal efficiencies were observed for FeCl₃+10 mg/L FSPS at a rate of 82% and for FeCl₃+5 mg/L PEL at a rate of 82%. These performances, which are obtained at the orginal pH of the wastewater (pH13±1), have changed significantly at different pH (Figure 3). At selected doses of Alum + FSPS above, the turbidity removal performance showed a significant increase in the pH range of 3-9 compared to the original pH and turbidity removal efficiencies increased from 50% to range 95-97%. The same situation also applies Alum + PEL used. But when FeCl₃ is used, turbidity removal performance at lower pH than 13 is lower (while 88-89% is reduced to 60-70%).
The most efficient COD removals were observed with Alum+FSPS and Alum+PEL in the pH value of 7 (Figure 3). At this pH, the COD removals were obtained 80% for Alum+40 mg/L FSPS and 78% for Alum+5 mg/L PEL. When FeCl₃ was used, the COD removal efficiency at both the original pH and at the different pH values were found to be in the range of 68-81%.

The SS removal efficiency was different between the use of Alum and the use of FeCl₃. When Alum+FSPS and Alum+PEL were used, the SS removal efficiencies were observed as 61% and 50%, respectively, whereas with FeCl₃, the removal efficiencies with both FSPS and PEL doses were 93-94%. The SS value of wastewater decreased from 1280 mg/L to 90 mg/L.

In the case of using Alum for oil-grease removal, 65-69% efficiency was obtained with both flocculants. But the Oil-grease yield of FSPS flocculant with FeCl₃ was 83%. On the other hand, PEL with FeCl₃ provided 69% oil-grease removal.
4. Conclusion

In this study, PS plastic waste was sulfonated and FSPS flocculant was synthesized. The synthesized materials were used in coagulation-flocculation treatment of waste plastic washing wastewater. Based on the nature of this physicochemical treatment method, the turbidity removal performance was taken as the basis and the treatment condition was determined accordingly.

For PS washing wastewater, Alum and FSPS are recommended as successful at pH 9. The turbidity, COD, SS and oil-grease removal efficiencies are similar for varying FSPS doses. Optimal coagulant, flocculant dose and pH are determined as 1000 mg/L Alum, 20 mg/L FSPS at pH 9 (96%), respectively. In these conditions, the turbidity value of 3453 NTU of raw wastewater decreases to 151 NTU. In addition in these conditions, COD, SS and Oil-grease removal was found 78%, 94% and 84%, respectively.

As a result, it has been determined that the obtained flocculant is efficient in treatment. The material recovery from waste plastic and its use in treatment reveals the importance of this study. In the subsequent stages of this study, the synthesized flocculant will be used for different types of wastewaters.

Acknowledgement

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References


Thermoplastic Wastes Pyrolysis Char in the Epoxy Composite as Filler

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Keywords: Mixed thermoplastics, pyrolysis, char, epoxy composite

Abstract

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

1. Introduction

Pyrolysis degrades the solid waste into gaseous, liquid and solid fractions. In most of the plastic pyrolysis studies, either single type of plastic, or mixture of plastics, especially PE, PP, PS and PVC types of plastics, have been pyrolysed. Generally, gas and liquid fraction percentage and quality differences have been discussed (Adrados et al, 2012; Arabiourrutia et al., 2012; Williams and Slaney, 2007). Pyrolysis gases and liquids have been commonly used either as fuel or as feedstock. However, use of pyrolysis solid fraction, char, is rather rare. The most common lab-scale trials are on its utilization as adsorbent (Pellera and Gidarakos, 2015).

Composites are the materials prepared by combining the materials from the same or different classes to obtain a single product. Especially polymer composites have advantages over other materials such as high strength, thermal stability, hardness etc. Moreover, they are lighter than metals and they can be processed at much lower temperatures (Şahin, 2000; Ratna, 2007).

Thermoset resins, especially epoxy resins can be used in composite (ER) preparation, in protective surface covers, or can be used as adhesives. They have some advantageous properties such as hardening at low to high temperatures, high strength, adhesion, high chemical strength (URL1). By these properties, epoxy resins are preferred in composite materials as matrix material to number of types of additives such as carbon, glass, boron etc (URL1). These types of composites are used in space and aeronautical industries.

Recently, several studies investigated the utilization of plastics pyrolysis chars as filler (additive) in composites for HDPE, LDPE, PET, PP and PS type thermoplastic waste chars (Sogancioglu et al, 2017 a and b; Sogancioglu et al, 2016; Yel et al, 2017; Yel et al, 2016; Yucel et al, 2015; Ahmetli et al, 2013).

In waste management, separation of collected plastic wastes is a cost, time and labor consuming process. In this study, mixed thermoplastic wastes were directly pyrolysed without separation and/or pre-washing and the pyrolysis char was used as filler in epoxy composites.
composite (ER). Effect of filler dose and the pyrolysis temperature that it was obtained on the ER properties were investigated.

2. Materials and Methods

Thermoplastic wastes were collected from municipal waste separation center, main impurities (paper, etc) were removed and they were crushed to less than 8 mm. Batch pyrolysis was applied under inert (nitrogen) atmosphere at 5°C/min heating rate. At the end of pyrolysis the solid residue remained in the reactor was collected as char sample. In the composite matrix DGEBA type commercial epoxy resin-NPEL128 (EEW 190 g/eq), Epamine PC17 curing agent (Konuray Chemical Co) and 2,4,6-tris (dimethylaminomethyl) phenol (Sigma-Aldrich) accelerator were used. ER production method reported by Sogancioglu et al, (2017a) was applied.

Besides filler or additive type, its particle size and homogeneous distribution are important especially for better mechanical properties of the composite. To achieve this, first, Pyrolysis chars (particle size<63µm) obtained at different temperatures (300-700°C) were sieved through stainless steel sieves suitable to ASTM standards. Char samples were added as filler to epoxy resin matrix at varying (10, 30 and 50%) dosages and mixed with Heidolph Type RZR1 mechanical mixer. The homogeneous dispersion of char filler was further improved in ultrasonic bath. Then epoxy hardener and accelerator were added, mixed and filled to mold which fits ASTM D638 standard. After 1 day drying at room temperature, stepwise curing was applied from 40 to 120°C.

Electrical conductivities of the composites were measured by four-point probe technique. Shore Durometer TH 210 tester was used for measuring hardness of the composite. The stretch resistance properties were determined by the Stretch and Pressing Equipment TST-Mares/TS-mxe. Thermogravimetric analyses (TGA) were performed using a TGA analyzer, under nitrogen atmosphere at atmospheric pressure.

3. Results

SEM images of mixed plastic waste pyrolysis chars are indicated in Figure 1. Increased pyrolysis temperature resulted in higher decomposition in plastics and more homogeneous particles were observed. Non-degraded polymer particles were seen at pyrolysis char sample of 300°C but these disappeared at 700°C pyrolysis. Some non-polymeric impurities originating from the dirt onto the waste plastics were also observed, but their quantities reduced with increasing pyrolysis temperature (Figure 1).

<table>
<thead>
<tr>
<th>300 °C</th>
<th>500 °C</th>
<th>700 °C</th>
</tr>
</thead>
</table>

**Figure 1.** Mixed plastic waste pyrolysis char SEM images for different pyrolysis temperatures.
SEM images of Reference composite and composites with char additives are given in Figure 2. As char pyrolysis temperature and char dosage in the mixture increased, surface roughness changed. Surface adhesion seems better for 500°C char-added composite mixtures. Better surface adhesion means better elasticity modulus, which was verified in Table 1.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>%10</th>
<th>%30</th>
<th>%50</th>
</tr>
</thead>
<tbody>
<tr>
<td>300°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>700°C</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2. SEM images of Reference composite (neat ER) and composites with char additives

Mechanical, electrical, thermal and water absorption properties of the composites are compared in Table 1. Increased pyrolysis char filler dosage decreased the % elongation at break for all pyrolysis temperatures and all of the values were low as compared to neat ER. 500°C and greater pyrolysis char filler at 10% dosage resulted in increase in tensile strength of the composites (Table 1). Similarly, elasticity modulus and hardness values of composites were increased by char filler. These indicated that char filler can improve physical properties of ER, char pyrolysis temperature and dosage have influence on the composite quality and pyrolysis char filler have potential to improve mechanical properties depending on the
pyrolysis temperature and char dosage.

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

<table>
<thead>
<tr>
<th>Pyrolysis Temp. (filler, weight%)</th>
<th>Elongation at break %</th>
<th>Tensile strength, MPa</th>
<th>E-modulus, GPa</th>
<th>Hardness Shore D</th>
<th>Electric conductivity S/cm</th>
<th>IDT</th>
<th>SDT</th>
<th>Water absorp. rate, mg/g comp/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat ER</td>
<td>0.721</td>
<td>86</td>
<td>6.2</td>
<td>80</td>
<td>10&lt;sup&gt;-14&lt;/sup&gt;</td>
<td>125</td>
<td>275</td>
<td></td>
</tr>
<tr>
<td>ER/Mixed Plastic waste composites</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300ºC (10%)</td>
<td>0.759</td>
<td>80</td>
<td>8.1</td>
<td>80</td>
<td>1.94×10&lt;sup&gt;-6&lt;/sup&gt;</td>
<td></td>
<td></td>
<td>0.0111</td>
</tr>
<tr>
<td>300ºC (30%)</td>
<td>0.651</td>
<td>73</td>
<td>7.4</td>
<td>81</td>
<td>1.88×10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td></td>
<td></td>
<td>0.0140</td>
</tr>
<tr>
<td>300ºC (50%)</td>
<td>0.472</td>
<td>54</td>
<td>5.5</td>
<td>79</td>
<td>2.01×10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td></td>
<td></td>
<td>0.0486</td>
</tr>
<tr>
<td>400ºC (10%)</td>
<td>0.559</td>
<td>81</td>
<td>9.3</td>
<td>79</td>
<td>2.13×10&lt;sup&gt;-6&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400ºC (30%)</td>
<td>0.487</td>
<td>78</td>
<td>7.3</td>
<td>80</td>
<td>1.39×10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>400ºC (50%)</td>
<td>0.445</td>
<td>75</td>
<td>7.7</td>
<td>80</td>
<td>1.56×10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>500ºC (10%)</td>
<td>0.585</td>
<td>96</td>
<td>10.0</td>
<td>80</td>
<td>1.45×10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>195</td>
<td>290</td>
<td>0.0184</td>
</tr>
<tr>
<td>500ºC (30%)</td>
<td>0.502</td>
<td>80</td>
<td>9.5</td>
<td>82</td>
<td>2.82×10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>235</td>
<td>335</td>
<td>0.0143</td>
</tr>
<tr>
<td>500ºC (50%)</td>
<td>0.394</td>
<td>85</td>
<td>8.9</td>
<td>83</td>
<td>1.25×10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>285</td>
<td>380</td>
<td>0.0282</td>
</tr>
<tr>
<td>600ºC (10%)</td>
<td>0.438</td>
<td>106</td>
<td>7.8</td>
<td>82</td>
<td>1.04×10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600ºC (30%)</td>
<td>0.351</td>
<td>88</td>
<td>9.0</td>
<td>82</td>
<td>9.08×10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600ºC (50%)</td>
<td>0.307</td>
<td>72</td>
<td>9.1</td>
<td>81</td>
<td>1.79×10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>700ºC (10%)</td>
<td>0.474</td>
<td>81.6</td>
<td>9.5</td>
<td>83</td>
<td>2.77×10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td></td>
<td></td>
<td>0.0177</td>
</tr>
<tr>
<td>700ºC (30%)</td>
<td>0.437</td>
<td>77</td>
<td>9.6</td>
<td>84</td>
<td>1.32×10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td></td>
<td></td>
<td>0.0213</td>
</tr>
<tr>
<td>700ºC (50%)</td>
<td>0.346</td>
<td>56</td>
<td>6.4</td>
<td>85</td>
<td>1.67×10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td></td>
<td></td>
<td>0.0240</td>
</tr>
</tbody>
</table>

Neat ER is an insulating material (conductivity: 10<sup>-14</sup> S/cm). However, by the addition of plastics pyrolysis char filler, the material become semi-conductor with increasing conductivities (Table 1). Pyrolysis temperature affected the composite conductivities, however, as filler dosage increased, conductivities increased as well. At pyrolysis temperatures 500ºC or higher, aromaticity and carbonized material increase in the char content can be the reason for this (Eghlimi et al., 1999; Diakoumakos et al., 1995).

Besides these mechanical and electrical properties, thermogravinetry also indicated that by adding char filler, more durable composites were produced such that as filler dose increased, FDS and SDS temperatures increased as compared to neat ER (Table 1).

As porous structure on the char surface increased, water absorption increases and pyrolysis temperature affects the pore size distribution in chars. The char fillers have 22-35 Å pore size distribution. In spite of this range, composites with filler has very low water absorption rates. Increased filler dosage (50%) increased water absorption rate. The composites reach water saturation level in around 210-306 hours.

Plastics and other recyclable materials are not being allowed to be landfilled in most of the developed countries. Whereas in many developing countries they have been directly sent to landfill sites due to its low cost. Landfilling of plastic wastes has number of adverse environmental effects besides their USD167/ton cost (EU Directive 94/62/EC, 2003). On the other hand, recycling cost of plastic wastes (USD422/ton) is not lower as reported in the same directive. The highest portion of this cost belongs to collection, transportation and separation cost of plastic wastes. Separation at source is the problem which has not been completely solved yet in all over the world. The high cost of plastic recycling unfortunately reduces the economic value of its recycled products. Another alternative for plastic wastes is incineration, which has been applied for many years in most part of the world, and which never been performed due to toxic, hazardous and detrimental effects of number of emitted substances. Considering the cost of necessary precautions for prevention of emission of such
substances. Incineration cost was reported as USD233/ton (EU Directive 94/62/EC, 2003). These indicated that, the cost of even the simplest disposal techniques is still high. Therefore, it is necessary to develop new technologies and/or approaches to convert them to economical values in order to reduce these disposal costs. This study developed a new approach to obtain new products from mixed plastic wastes.

Conclusions

The study indicated that, mixed thermoplastics can directly be pyrolysed to use char as ER filler to obtain good quality semi-conductor composites. Considering the costs and carbon footprints of plastic waste transport and separation processes, it is suggested that the solution which does not need separation of plastic types is favorable. When mixed plastic wastes are pyrolysed, the pyrolysis liquid and gas products will contain numbers of organic structures which can be utilized either as fuel or as feedstock in many types of industries. These products characterization is the subject of another study of the authors. The mixed thermoplastics pyrolysis solid product, namely char, generally referred to as pyrolysis residue. However, as a result of this study, it is now a feedstock to be used in durable, sturdy, tough, semi-conductor epoxy composite production.

Acknowledgement

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Effects of some Cations on Arsenic Removal from Groundwater by Air-Injection Electrocoagulation Reactor

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Keywords: Cation effect, Al ball electrode, Optimization, Reactor Design

Abstract

Combined effects of calcium, iron, magnesium and manganese on the removal of arsenic from groundwater were investigated and the operating conditions were optimized. Effects of cations on the removal efficiency of arsenic (100 µg/L As (III) + 100 µg/L As (V)) at current density of 0.15 A, Al ball size of 7.5 mm, anode height in the EC reactor of 5 cm, pH 7.5 and air flow rate of 6.0 L/min in the air injected EC reactor were evaluated with Box-Behnken statistical experiment design. Iron (0.5-4.5 mg/L) increased the removal of arsenic even at relatively low concentrations. The rest of the cations showed noticeable effect on the removal efficiency. The obtained results indicated that maximum removal efficiency of arsenic and minimum operating cost at the optimized conditions (CCa: 305 mg/L, CMg: 42 mg/L, CFe: 3.3 mg/L, CMn: 2.34 mg/L ve tEC: 16.83) were observed as 99.9% and 0.03318 $/m³, respectively.

1. Introduction

Globally, groundwater one of the most important source of water supply. But it is not safe for drinking purposes as arsenic contamination of groundwater is a widespread occurrence affecting vast regions in the world. Arsenic contamination of natural waters occurs naturally through weathering and dissolution of arsenic containing minerals, also human activities [1]. Long-term drinking water containing arsenic causes various cancer as well as skin lesions, hyperkeratosis, and melanosis [2]. Due to its high toxicity to human health, the World Health Organization (WHO) lowered limit of arsenic in drinking waters from 50 µg/L to 10 µg/L [3]. Therefore, arsenic removal from groundwater has become an issue that attracts great interest from an environmental perspective.

In recent years, EC has been successfully employed to removal of arsenic from groundwater. The previous studies mainly focused on only arsenic content of the groundwater. However, those waters does not agree with the chemical composition of actual groundwater. In real groundwater, large amount of coexisting anions and cations are present depending on the environment in which groundwater source is located. These ions are
known to interact with metal hydroxides surfaces and may compete with arsenic for adsorption. Anions and cations might affect negatively or positively influence the adsorption of arsenic [4]. While some anions (PO₄³⁻, SO₄²⁻, SiO₃⁻, HCO₃⁻) can compete strongly with arsenic for metal hydroxide surfaces, otherwise (Ca²⁺, Mg²⁺, Fe²⁺, Al³⁺, Mn²⁺, Na⁺) cations promote the removal of arsenic.

In this study, an air fed new EC reactor is designed which has specifications of compactness, easy to use, accommodating of more anode electrodes with higher surface areas and providing better removal efficiency. A new EC reactor is used for both arsenic removal from groundwater and for investigation of cations (Ca, Mg, Fe and Mn) effects on arsenic removal. Also, full a three level Box-Behnken experimental design variables with response analyses (effluent arsenic concentration, arsenic removal efficiency and operating cost) were studied with the new EC reactor data. Effects of cations concentrations and operating time on removal were analyzed.

2. Materials and Methods

2.1. Groundwater Characteristics

The groundwater was obtained from a well in the province of Kocaeli, Turkey. Quality of the groundwater were determined as a pH of 7.5, electrical conductivity of 1.3 mS/cm, sodium of 22 mg/L, calcium of 152 mg/L, magnesium of 15 mg/L, chloride of 127 mg/L, sulphate of 94.2 mg/L, nitrate of 2 mg/L, total Si of 10 mg/L, CaCO₃ of 260 mg/L, total dissolved solids of 528 mg/L, and total organic carbon of 5 mg/L. Iron, manganese, phosphorus, and arsenic in the groundwater were not identified. The groundwater sample containing total arsenic of 200 μg/L (100 μg/LAs(III) + 100 μg/LAs(V)) was daily prepared by dissolving sodium arsenate (Na₂HAsO₄·7H₂O) for As(V) and sodium arsenite (NaAsO₂) for As(III). Then, the stock solutions of cations were prepared by dissolving pre-weighted amount of reagents of magnesium, calcium, iron and manganese stock solutions are prepared from MgCl₂, CaCl₂, Fe₂SO₄ and MnCl₂, respectively. All chemical species present in groundwater were determined with standard methods [APHA]. The arsenic concentration in the groundwater were determined by an inductively coupled plasma-optical emission spectrometry (ICP-OES) after and before the experiments. The concentrations of cations (Ca²⁺, Mg²⁺, Mn²⁺, Fe²⁺ and Na⁺) and anions (NO₃⁻, SO₄²⁻, PO₄³⁻ and Cl⁻) were measured by ICP-OES and by ion chromatography (IC) for the groundwater, respectively. TOC and turbidity were determined by TOC analyzer and turbidity meter. Total dissolved solid was measured by Mettler Toledo Seven Go.
2.2. Experimental set up and analytical procedure

Figure 1. shows the novel EC reactor with an air-injection unit used in this study. The novel EC reactor and experimental set up were reported in the earlier study [5]. The groundwater (800 mL) containing a total of arsenic and different concentrations of cations were placed into the EC reactor for an experimental run. The operating parameters (current density of 0.15 A, Al ball size of 7.5 mm, anode height in the EC reactor of 5 cm, pH 7.5 and air flow rate of 6.0 L/min) were adjusted according to our previous works and the experiment was started. The samples collected at pre-established intervals were filtered through a 0.45 μm Millipore membrane, then arsenic and cations concentrations were measured by ICP optical emission spectrometry (Shimadzu HIC 20A).

2.3. Experimental design and statistical analysis

The Box-Behnken experimental design (BBD) was used for the optimization of arsenic removal from groundwater in order to obtain maximum removal efficiency and minimum operating cost as well as investigate the effect of independent process variables on arsenic removal. In this model, five independent variables, calcium ($x_1$), magnesium ($x_2$), iron ($x_3$), manganese ($x_4$) concentrations and operating time ($x_5$) were selected and each variable was varied over three levels (Table 1). As shown in Table 1, each independent variable was conducted at three different levels, coded as -1, 0 and +1 for low, middle and high concentrations, respectively. Other operating parameters such as current
density, Al ball size, anode height in the EC reactor, pH and air flow rate were kept constant. According to BBD matrix generated by Design Expert software (Trial version 8.0.4.1), total 46 experimental run were performed. The experimental runs were randomized to maximize the effects of unexplained variability in the observed responses such as effluent pH (PHf), arsenic removal efficiency (Re, %), electrode consumption (ELC, kg/m³), energy consumption (ENC, kWh/m³), operating cost (OC, $/m³), sludge formation (Wsludge, kg/m³) and arsenic removal capacity per dissolved mg aluminum anode (qe, µg As/C or µg As/mg Al).

### Table 1. Independent variables and levels for three level factorial study of arsenic removal

<table>
<thead>
<tr>
<th>Independent variables</th>
<th>Levels of independent variables</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-1</td>
</tr>
<tr>
<td>(X_1) : C(_{Ca}) (mg/L)</td>
<td>125</td>
</tr>
<tr>
<td>(X_2) : C(_{Mg}) (mg/L)</td>
<td>15</td>
</tr>
<tr>
<td>(X_3) : C(_{Fe}) (mg/L)</td>
<td>0.5</td>
</tr>
<tr>
<td>(X_4) : C(_{Mn}) (mg/L)</td>
<td>0.5</td>
</tr>
<tr>
<td>(X_5) : t(_{EC}) (min)</td>
<td>8</td>
</tr>
</tbody>
</table>

### 3. Results and discussion

#### 3.1. Effect of manganese on arsenic removal

Arsenic removal efficiency can influence positively with manganese species due to its ability to adsorb/coprecipitate As (V) on manganese dioxide (MnO\(_2\)) and manganese hydroxide (Mn(OH)\(_2\)) surfaces. The removal efficiency found as 98% for 4.5 mg/L of manganese concentration at 2.5 mg/L of iron dosage when the removal efficiency decreased to almost 95% for 2.5 mg/L of manganese concentration. (Figure 2(b)-(e)-(f)).

#### 3.2. Effects of calcium and magnesium on arsenic removal

Calcium and magnesium can be present naturally in groundwater and it has significant impact on adsorption of anions and hardness of water. The Ca\(^{2+}\) cation may enhance the arsenate removal with the formation of calcium-aluminum-arsenate-hydroxide Ca\(_{Al_n}(OH)_{(3n-1)}\) (AsO\(_4\)) coprecipitate in EC process. Magnesium have also significant
impacts on precipitate formation and arsenic removal. In EC process, arsenic removal may occur coprecipitation with magnesium hydroxide flocks. The removal efficiency of arsenic increase with the increasing Ca$^{2+}$ concentration. **Figure 2(c)-(a)** demonstrates the effect of Ca$^{2+}$ concentration on arsenate removal. At the minimum Ca$^{2+}$ concentration of 125 mg/L arsenic removal efficiency observed as almost 94%, while the arsenic removal efficiency found as almost 98% at the maximum Ca$^{2+}$ concentration of 325 mg/L. The removal efficiency found as 98% for 225 mg/L of calcium concentration at 2.5 mg/L of iron dosage when the removal efficiency decreased to almost 96% at 1.5 mg/L of iron dosage (**Fig 2(c)**). In addition, the removal efficiency found as 98% for 325 mg/L of calcium concentration at 1.5 mg/L of manganese dosage when the removal efficiency decreased to almost 97.5% at 2.5 mg/L of magnesium dosage (**Fig 2(b)-(d)**).

3.3. Effects of iron on arsenic removal

At the beginning of the EC process, the iron competes with arsenic for adsorption sites of aluminum flocs. However, as the EC process proceeds the iron hydroxide formation and precipitation becomes more predominant which forms unused adsorption sites for arsenic. Hence, the presence of iron enhance the arsenic removal by EC process. The arsenic removal efficiency increased with the increasing iron concentration. Arsenic removal efficiency increased from 94% at 0.5 mg/L to 100% at 4.5 mg/L iron concentration (**Figure 2(f)**).

4. Conclusions

In the present study, forty-six experiments for the investigation of effects of cations on arsenic removal were carried out by the Box-Behnken experimental design in the EC process. Interactions of four different cations and operating time were considered. There was a positive effect on the removal efficiency as operating time increased the arsenic removal in the EC reactor using Al ball anodes. Likewise, arsenic removal efficiency increased with the increase in concentrations of especially iron, magnesium, calcium, and manganese. As a result, the maximum removal efficiency, arsenic adsorption capacity and minimum operating cost at 16.85 min of operating time were 99.9%, 11.14 μg As/mg Al, and 0.03318 $/m^{3}$ when concentrations of calcium, magnesium, iron, and manganese were 305 mg/L, 42 mg/L, 3.3 mg/L, and 2.34 mg/L, respectively. The results clarified that the EC reactor can remove arsenic effectively from groundwater which also contains cations.
Fig. 2. Contour plots showing the effects of (a) magnesium and calcium, (b) manganese and calcium, (c) iron and calcium, (d) iron and magnesium, (e) manganese and magnesium, (f) iron and manganese on percentage of As (V) removal.

5. References

Power-to-Gas (P2G) and applications: investigating the effect of hydrogen injection into the natural gas

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Keywords: Hydrogen production; Hydrogen recycling system; Power-to-Gas (P2G); Renewable energy

Abstract

Nowadays, due to concerns about environmental issues and the credibility of energy sources, power generation through the use of renewable energy sources has become increasingly important. In this paper, some of the conventional energy storage methods are first introduced and reviewed, and then the introduction of the new power emerging technology, called Power-to-Gas (P2G), is discussed. Finally, the impact of hydrogen injections into the natural gas (NG) pipelines (as one of the most important applications of P2G technology) will be investigated. This investigations is presented for different gas fields in Iran as case studies and the thermophysical properties of the gas mixture is calculated using AGA8 equation of state (EOS).

1. Introduction

In the recent years, the European energy policy has agreed on the increased integration of renewable energy (such as solar energy) sources in the energy system, and large efforts are being made to implement renewable energy. The increasing share of renewable energy sources, in most cases coupled with an absolute increase of production, includes as well as advantages, challenges and problems [1, 2].

Various energy storage systems are currently available on the market with extremely heterogeneous development stages. These range from for several decades established technologies such as pumped hydro storage power stations for large quantities or batteries for small storage quantities, through to technologies and systems which are currently in the development stage, such as rechargeable batteries or flywheels [3].

Each of these systems are faced with limitations and consequently it should select the best storage method depending on the geographic location and available resources in each area. In the meantime, various parameters will affect the selection of the appropriate method; some of the most important parameters can be named to: the capacity of the system, the efficiency of the system and the storage time (the time in which the stored energy can be saved). Table 1 provides a comparison of these parameters for different energy storage methods. Based on Table 1, the P2G technology responds well to all of the important parameters. P2G technology, while having a good energy efficiency, can meet low capacity (scale from kW) to high capacity (MW scale) with high storage time.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Storage capacity range (MW)</th>
<th>Efficiency (%)</th>
<th>Storage time range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Comparison of the different energy storage systems
### 2. An overview of the P2G technology

Power-to-Gas is a process in which electrical energy is converted into hydrogen or synthetic natural gas (SNG). A schematic of the P2G technology and its components is drawn in Fig. 1. As it can be seen in this figure, in the first step an electrolyzer is used to produce hydrogen from electrical energy. This energy can be supplied to the electrolyzer with either public electricity grid or renewable energy sources (but the emphasis in P2G technology is to expand the use of renewable energies). Currently, two different technologies are discussed for the electrolyzer: polymer electrolyte membrane (PEM) and alkaline electrolysis. The typical efficiency of an electrolyzer is about 60-70% [4]. In the second step of the P2G technology, the produced hydrogen can be used for various applications containing: storing in H₂ storage tanks, using as fuel of the no-emission clean cars, feeding into the NG pipelines, converting to the SNG (using by a methanation unit) and etc. For the methanation step in P2G technology, four moles of the produced hydrogen is combined with one mole of carbon dioxide (CO₂: which is one of the main greenhouse gases in environment) to obtain one mole of methane and two moles of steam. This process is known as Sabatier reaction and is an exothermic process (-0.045 kWh/mol) and requires high temperature and high pressure to produce a high amount of methane. The efficiency of such a reaction ranges from 75% to 80% [5]. Based on the mentioned contents, by using this technology, in addition to expanding the use of renewable energy sources, a huge step will be taken to reduce environmental pollution (through the use of environmental pollutants in the process of methanization).
3. The effect of the hydrogen injection into the NG

As it mentioned, the aim of the current study is to investigate the effect of the hydrogen admixing into the NG. As the first step, there need to calculate the thermophysical properties of the H$_2$+NG mixture. Accordingly, it should be used real gas EOSs. In current work, the thermophysical properties of the gas mixture are determined using well-known AGA8 EOS. The AGA8 EOS can be described as Eq. (1).

\[
Z = 1 + B\rho_m - \rho_r \sum_{n=13}^{19} C_n^* + \sum_{n=13}^{58} C_n^* D_n^* 
\]

In which, $Z$, $B$, $\rho_m$ and $\rho_r$ are compressibility factor, the second virial coefficient, molar density and reduced density, respectively. Also, $C_n^*$, $D_n^*$ and $K$ are coefficients of the AGA8 EOS. Details of AGA8 EOS and also it’s coefficients is available in ISO 20765-1:2005(E) standard [6].

The heating value of a substance, is defined as the amount of released heat during the combustion of a specified amount of it. The combustion equation for one of the NG components and also the amount of the molar heating value for NG mixture (J/mol) are expressed as Eqs. (3) and (4), respectively.

\[
C_a H_b O_c N_d S_e \left( a + \frac{b}{4} - \frac{c}{2} + e \right) O_2 \rightarrow aCO_2 + \frac{b}{2}H_2O + \frac{d}{2}N_2 + eSO_2 
\]
\[ H_m(T) = \sum_{j=0}^{N} x_j H_{m,j}(T) \] (4)

Where \( H_m \) and \( x_j \) are molar heating value of the gas mixture and mole fraction of the \( j \) component in gas mixture. Also, \( H_{m,j}(T) \) is molar heating value at temperature of \( T \) for the \( j \) component in the gas mixture and calculated using Eq. (5).

\[ H_{m,j}(T) = H_{m,j}(25 \, \text{°C}) - \sum_k v_k [h_{m,k}(T) - h_{m,k}(25 \, \text{°C})] \] (5)

Where, \( H_{m,j}(25 \, \text{°C}) \), \( v_k \), \( h_{m,k}(T) \) and \( h_{m,k}(25 \, \text{°C}) \) are molar heating value at temperature of 25 °C for the \( j \) component in the gas mixture, stoichiometric coefficient of the combustion reaction for the \( k \) component in combustion (reactors and products), molar enthalpy of the \( k \) component in the combustion reaction at temperatures of \( T \) and molar enthalpy of the \( k \) component in the combustion reaction at temperature of 25 °C, respectively.

In current paper, the investigations are applied to the various NG fields in Iran as case studies. The details of the mole fraction for these NGs are presented in Table 2.

Table 2. Mole fractions of the Iran’s NG fields (case studies)

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole fraction (%)</th>
<th>Kangan</th>
<th>Ghasho</th>
<th>Khangiran</th>
<th>Pars</th>
<th>Bidboland</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>90.04</td>
<td>79.08</td>
<td>98.6</td>
<td>87</td>
<td>80.01</td>
<td></td>
</tr>
<tr>
<td>C₂H₆</td>
<td>3.69</td>
<td>0.91</td>
<td>0.59</td>
<td>5.4</td>
<td>1.38</td>
<td></td>
</tr>
<tr>
<td>C₃H₈</td>
<td>0.93</td>
<td>0.36</td>
<td>0.09</td>
<td>1.7</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>I-C₄H₁₀</td>
<td>0.2</td>
<td>0.09</td>
<td>0.02</td>
<td>0.3</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>N-C₄H₁₀</td>
<td>0.29</td>
<td>0.18</td>
<td>0.04</td>
<td>0.45</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>I-C₅H₁₂</td>
<td>0.14</td>
<td>0.08</td>
<td>0.02</td>
<td>0.13</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>N-C₅H₁₂</td>
<td>0.08</td>
<td>0.07</td>
<td>0.02</td>
<td>0.11</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>N-C₆H₁₄</td>
<td>0.14</td>
<td>0.69</td>
<td>0.07</td>
<td>0.07</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>+C₇H₁₆</td>
<td>0.01</td>
<td>0</td>
<td>0</td>
<td>0.03</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>4.48</td>
<td>5.14</td>
<td>0.55</td>
<td>3.1</td>
<td>5.41</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>0</td>
<td>7.08</td>
<td>0</td>
<td>1.71</td>
<td>8.41</td>
<td></td>
</tr>
<tr>
<td>H₂S</td>
<td>0</td>
<td>6.32</td>
<td>0</td>
<td>0</td>
<td>3.03</td>
<td></td>
</tr>
</tbody>
</table>

4. Results

In this section, attention has been paid to investigate the effect of the 1-10 vol.% hydrogen injection into the NG (with various compositions for NG fields in Iran) on the compressibility factor and heating values of the gas mixture.
As samples, the results of the 1 vol.%, 5 vol.% and 10 vol.% hydrogen injection effect on the compressibility factor are presented in Table 3. As it can be seen in this table, the hydrogen injection into the natural gas causes an increase in compressibility factor. For example, increasing hydrogen concentration from 1 vol.% to 10 vol.%, the compressibility factor of the gas mixture increases 1.038%, 1.042%, 0.933%, 1.149% and 0.930% for Kangan, Ghasho, Khangiran, Pars and Bidboland, respectively. Also, the results showed that for each case study, the compressibility factor increases as a linear function by addition of the hydrogen to the NG.

**Table 3. The effect of the 1-10 vol.% hydrogen injection into the Iran’s NG fields on the compressibility factor**

<table>
<thead>
<tr>
<th>Hydrogen injection amount (vol.%)</th>
<th>Kangan</th>
<th>Ghasho</th>
<th>Khangiran</th>
<th>Pars</th>
<th>Bidboland</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%</td>
<td>0.963</td>
<td>0.960</td>
<td>0.965</td>
<td>0.957</td>
<td>0.968</td>
</tr>
<tr>
<td>5%</td>
<td>0.967</td>
<td>0.964</td>
<td>0.969</td>
<td>0.962</td>
<td>0.972</td>
</tr>
<tr>
<td>10%</td>
<td>0.973</td>
<td>0.970</td>
<td>0.974</td>
<td>0.968</td>
<td>0.977</td>
</tr>
</tbody>
</table>

The higher heating value (HHV) of hydrogen and NG is 13 MJ/Nm³ and 40 MJ/Nm³, respectively [4]. Accordingly, the energy density of hydrogen is about 3 times lower than that of NG. Variation of HHV and LHV for different NG fields (with mole fraction described in Table 2) by injecting 1-10 vol.% hydrogen is displayed in Fig. 2. Analyzing the results of this figure shows that by increasing hydrogen concentration from 1 vol.% to 10 vol.%, the HHV of the gas mixture decreases 8.75%, 5.835%, 6.157%, 6.210% and 6.631% for Ghasho, Bidboland, Khangiran, Kangan and Pars, respectively.

The only disadvantage of the hydrogen admixing to the NG is reduction of the heating value but it causes following benefits:

- The final available amount of gas has been increased: this is useful for peak-shaving.
- The pollution emissions of the NG+H₂ is lower than just NG: this means that we have a cleaner fuel.
Fig. 2. The effect of the 1-10 vol.% H₂ injection into the NG on, (A) higher heating value, (B) lower heating value.

5. Conclusion

P2G technology, a novel technology for converting different power sources into the hydrogen and other gas energy carriers, attracts many attentions all over the world. In current paper the efforts have been paid to present an overview about P2G technology. Finally, the effect of hydrogen admixing produced by P2G technology has been investigated on the thermophysical properties of various NGs in Iran.

References


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

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

Abstract

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

1. Introduction

Reducing water losses, energy losses and carbon dioxide emissions are among the primary goals for the implementation of sustainable water supply systems. Most of the water supply systems exhibit excess water pressure where break pressure tanks, reservoirs or pressure reducing valves are commonly used to reduce the excess pressure. Energy recovery from excess water pressure in water distribution networks (WDNs) is a new subject of interest (Fontana et al. 2012, Jain and Patel, 2014). Excess pressure in WDNs causes excess water losses and frequent pipe breaks besides reducing the service life of the WDN. Saving water implies saving energy that is used to abstract, treat and pump the water to the WDN. In recent years, the use of PAT has attracted considerable interest for reducing excess pressure besides energy recovery (Ramos and Borga 1999, Giugni et al. 2009, Samora et al. 2016a,b). Recently, a full-scale PAT system was implemented and operated at Anfaş WDN of Antalya city within the scope of a research project (Muhammetoglu et al. 2017, 2018). With the implementation of this PAT system, excess pressure of approximately 1 bar have been reduced that led to considerable reduction in water losses besides an average power production of 2.37 kWh for an average flow rate of 165 m³/h. After this successful application of PAT system, an alternative pilot study area (PSA), Kaleici, was investigated for energy recovery potential using a PAT system and its initial findings were presented in this study.

2. Materials and Methods

Kaleici is a famous tourism destination located at the center of Antalya city. The topography is highly changing at Kaleici PSA where the elevations vary between 0 to 40 meters above the mean sea level (Figure 1) which causes excess water pressure mainly at the low elevations of the WDN. PSA is a single inlet district metered area (DMA) that is isolated from the rest of WDN of Antalya city. Flow rates and water pressures are continuously measured online at the SCADA station located at the entrance of the PSA in addition to five online pressure measurement points (PMP) within the WDN, located at
different elevation levels (Figure 1). The US-EPA EPANET hydraulic model was applied to the PSA to obtain optimum operational pressure at the inlet of DMA and to determine excess water pressure levels. The physical configuration of WDN and other relevant data sets required for EPANET model were obtained from Antalya Water and Wastewater Authority, ASAT (Figure 2).

3. Results

EPANET model was initially calibrated for Hazen-Williams pipe roughness coefficient and the predicted pressure values were in good agreement with field measurements. The hydraulic model application results for the period of August 20-25, 2015 is presented for
minimum and maximum pressure conditions at Figures 3 and 4. This period presents the peak season for maximum water consumption. Additionally, the hydraulic model application results for the period of January 14-19, 2016, which represents the off-season months, is presented for minimum and maximum pressure conditions at Figures 5 and 6. The minimum and maximum inlet pressure values and flow rates were measured at SCADA station, located at the entrance of the Kaleici DMA.

Figure 3. Spatial distribution of pressure levels at WDN at minimum inlet pressure condition in peak season (August 24, 2015 time: 10:55, pressure: 30.88 m, flow rate: 148,375 m³/h)

Figure 4. Spatial distribution of pressure levels at WDN at maximum inlet pressure condition in peak season (August 24, 2015
time: 05:15, pressure: 42.44 m, flow rate: 75.6 m³/h)
Figure 5. Spatial distribution of pressure levels at WDN at minimum inlet pressure condition in off-season (January 15, 2016 time: 12:10, pressure: 31.43 m, flow rate: 90 m³/h)

Figure 6. Spatial distribution of pressure levels at WDN at maximum inlet pressure condition in off-season (January 19, 2016 time: 05:15, pressure: 42.94 m, flow rate: 68.63 m³/h)
According to Technical Regulations of Bank of Provinces, the minimum water pressure to be maintained within the WDNs in Turkey is set as 20 m water column. Taking into consideration the national regulation criteria, the excess water pressure heads were determined as 5 m for the peak season months (June, July, August, September and October 2016 and May 2017) and 9 m for the off-season months (November and December 2016, January, February, March and April 2017). The average power production values were obtained as 0.71 and 1.32 kWh for peak season and off-season months, respectively, whereas the flow rates passing through PAT system were determined as 87.58 and 88.75 m³/h for peak season and off-season months, respectively. The estimated temporal variations of flow rate passing through PAT system and the power production were presented at Figure 7 for January 2017. The average efficiency of PAT system was assumed as 60% based on the results obtained from Anfaş WDN. The potential energy recovery of Kaleici PSA was less than the full-scale application at Anfaş WDN (Muhammetoglu et al, 2018) due to low flow rates and low levels of pressure reduction at Kaleici PSA. Based on these initial findings, a cost-benefit analysis is required to evaluate the pay-back period of a possible PAT system implementation at Kaleici PSA and to help decision makers to give a final decision on its application.

![Figure 7. The estimated temporal variations of flow rate passing through PAT system and power production for January 2017](image)

4. Conclusion

PAT systems are efficient for reducing leakage but also for recovering the energy dissipated in reduction of excess water pressure. Therefore, they are expected to gradually replace, if feasible, the traditional application of PRV that implies energy losses. Hydraulic modelling of water distribution networks based on online field measurements of flow rates and water pressures is a powerful tool to predict pressure level variations all over the year. Consequently, excess water pressure levels can be predicted and the expected energy recovery can be calculated. The efficiency of the PAT system for energy production can be estimated based on similar real applications. As a result, hydraulic modelling and real application of PAT systems are vital for the evaluation of energy recovery potential.
The Impact of Supplying Information and Awareness Raising on Public Attitude for Acceptance of Grey Water Reuse in Istanbul
Abstract

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

1. Introduction

Segregation of domestic wastewater at the source is one of the best options for recycling and reuse of valuable materials embedded in domestic wastewater. Grey water is the stream which will result from such segregation regardless of the type of separation used. Containing all but toilet wastewater, grey water consists of wastewater from different washing functions in the households like bath tubs/showers, wash basins, laundries, kitchen sinks and dishwashers. As grey water constitutes 75% by volume and contains lesser amounts of pollutants as compared to conventional domestic wastewater, reclamation and reuse of this renewable alternative source presents an obvious benefit [1]. Recycling grey water can help mitigate the growth in the demand for pristine water from natural resources. Although different types of grey water may show variability in terms of constituents [2], non-potable reuse of grey water has been commonly recognized for various end uses including toilet flushing, municipal uses, landscaping, and irrigation, etc.[3-11] in various location of the world.

Although treating grey water for reuse as an alternative water source to almost any high-quality demanding end use is technically possible, positive public opinion and acceptance by consumers is one of the key elements in the success for full scale practice [12]. Furthermore, positive opinion and acceptance necessitates awareness in the subject matter and must be based on sound information, in this case about grey water and its management. This work was undertaken to investigate awareness and attitude of the public, and the impact of supplying information upon acceptance of grey water reuse. The paper will report the results of the survey conducted in the Turkish megacity Istanbul, focusing on present awareness and willingness of participants to use reclaimed grey water along with changes in their perception and level of acceptance after being informed about the subject matter, mostly focusing on sources of grey water, possible final uses and economic considerations.

2. Materials and Methods

This preliminary survey of 30 questions was run in Istanbul, Turkey with 227 participants on a face to face basis to be able to supply information and to directly answer any questions that they may pose. The questions were directed toward assessing the opinion of participants about their present awareness regarding recycling/reuse of grey water, their willingness to install grey water separation systems, and acceptance for using treated grey water in daily life. After finishing the entire questionnaire, participants were provided with a standard piece of information on grey water and 17 of the questions were repeated for the second time to assess the effect of supplying information. Meanwhile, questions from the
participants were answered. The assessment was mainly based on counts and percentages of possible choices. Changes in attitudes were calculated based on the difference between counts of selected choices as indicated in the first (before) and the second (after) runs. The participants’ profile is summarized in Table 1.

3. Results and Discussion

Table 1 summarizing the demographic data indicates that out of 227 participants, 46% was female and 54% was male. The largest segment of the survey sample was from young population with ages below 18 and between 18-34 years. 91% of the participants were people who received a university degree or equivalent and about 3% who were still working to get a university degree. The highest ranked occupation was engineering with 33%, followed by educational professionals, self-employed and administrative staff. Occupations with less than 5% was classified as other. Most of the participants with 93% live in urban areas, while only 7% live in rural areas and 46% of the entire participants have a connection to rural life.

<table>
<thead>
<tr>
<th>Demographic Data</th>
<th>No.</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gender</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Female</td>
<td>104</td>
<td>46</td>
</tr>
<tr>
<td>Male</td>
<td>123</td>
<td>54</td>
</tr>
<tr>
<td>Occupation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Engineering</td>
<td>75</td>
<td>33</td>
</tr>
<tr>
<td>Educational Professional</td>
<td>43</td>
<td>19</td>
</tr>
<tr>
<td>Owner/self-employed</td>
<td>30</td>
<td>13</td>
</tr>
<tr>
<td>Administrative work</td>
<td>22</td>
<td>10</td>
</tr>
<tr>
<td>Other</td>
<td>57</td>
<td>25</td>
</tr>
<tr>
<td>Educational Level</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Less than high school</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>High school</td>
<td>18</td>
<td>8</td>
</tr>
<tr>
<td>2-years degree</td>
<td>11</td>
<td>5</td>
</tr>
<tr>
<td>Undergraduate</td>
<td>145</td>
<td>64</td>
</tr>
<tr>
<td>Master</td>
<td>36</td>
<td>16</td>
</tr>
<tr>
<td>PhD</td>
<td>14</td>
<td>6</td>
</tr>
<tr>
<td>Urban / Rural</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Urban area</td>
<td>211</td>
<td>93</td>
</tr>
<tr>
<td>Rural area</td>
<td>16</td>
<td>7</td>
</tr>
</tbody>
</table>

The participants were first asked to rank their awareness regarding the reuse of the wastewater on a scale from 1 (lowest) to 5 (highest). 19% were not familiar at all to the reuse of wastewater, and the majority was moderately familiar with a typical scale of 3. Figure 1 presents awareness about water related terms, which revealed that the participants were familiar with the terms potable water and wastewater by 88 and 90% respectively, however, recognized the term non-potable water with a smaller percentage. Regarding grey water, 47% never heard of this term before and 24% heard about it but they were not sure of the meaning, indicating that the level of knowledge about this segregated wastewater stream was low, implying that its potential reuse as an alternative water source would be limited.

![Fig 1. Awareness regarding water-related terms](image-url)
The participants were asked about their opinion regarding segregation and reuse of greywater focusing upon the use of two different water supply streams (potable and non-potable) in the household, possible benefits of reuse of greywater, and its impact upon the environment and water resources, both before and after sharing information. Figure 2 shows acceptances were considerable to start with, and providing information improved public opinion by 21-28%.

![Figure 2. Opinion about grey water and reuse](image)

Figure 2. Opinion about grey water and reuse

Figure 3 presents the willingness of participants regarding the installation of greywater separation systems at their homes. Before sharing information, 67% of the participants said they would like to install this system to protect the environment while about 50% said they would like to construct their new homes with a greywater separation system. The percentages increased to 86% and 79% after supplying information. Figure 3 shows further that economics is an important aspect in terms of acceptance, as the survey has shown that the percentage of agreement increased by almost two fold, from 40% to 79%, if it was offered for free.

![Figure 3. Willingness to pay for installing grey water separation systems](image)

Figure 3. Willingness to pay for installing grey water separation systems

Regarding acceptance towards different origins of greywater, at least one of the household greywater sources was accepted by the participants for reuse with a range of 39-65% to start with, which increased to 73-82% after sharing information, as shown in Figure 4.

Where to reuse greywater is a critical matter, and it depends on the willingness and perception of the users. Figures 5-8 present acceptances for using treated greywater in and around households, agricultural and landscape irrigation, and for industrial products, both before and after providing information.
Figure 4. Sources of greywater for reuse in households

Figure 5. Impact of supplying information on the acceptance of using treated grey water in and around households

Figure 6. Impact of supplying information on the acceptance of using treated grey water in agricultural irrigation

Figure 7. Impact of supplying information on the acceptance of using treated grey water in landscape irrigation

Toilet flushing ranked the highest before and after sharing information with 79% and 92% respectively among choices shown in Figure 5, and washing cars ranked the second, showing high percentages which increased after providing information. The reuse of grey water in swimming pools was the choice which was least accepted by 22% of the participants and about 42% of them were neutral. The low percentage for swimming pools
might be attributed to concerns to come in contact or ingest a treated wastewater stream, which was improved to 35% after supplying information.

Before sharing information, regarding using grey water for irrigational purposes, participants were more conservative to accept crops that will be consumed without receiving any treatment, like uncooked vegetables with 25%. Fruits grown on soil and cooked vegetables received about 40%, while non-food crops were the highest preferred choice by 71%. This is most probably due to health concerns regarding the chances of crops getting in contact with a treated wastewater stream to possibly end up with a non-hygienic product. After providing information however, the percentages for all the choices improved and reached 41-86%.

In case of irrigating green areas with treated grey water, the percentages in the first run were in a range between 63-75%, which were also considerable, while in the second run, the acceptance level increased 80-90%. Preference of the participants were the same in both the first and the second runs, and indicated home gardens, parks and picnic areas as the most accepted choices.

Regarding daily life use, 57% accepted to wear clothes produced from cotton irrigated with treated grey water as shown in Figure 8. To start with, it was highly rejected to drink juice or consume sugar produced from plants irrigated with treated grey water. However, total rejection decreased upon supplying information. It was observed in the face to face interviews that psychological concerns comprised a significant obstacle in terms of applying grey water in daily life uses.

As the survey also indicated, supplying information to the public increases their awareness and motivation in using treated grey water, either directly or indirectly. The major responsibility lies with state and local authorities to take the lead, as well as NGOs, to increase public awareness and to provide support to communities technically, economically and psychologically.

All in all, for all questions in the survey there was an increase in public acceptance ranging from 17 to 63% showing the positive impact of supplying information to the community in terms of enhancing willingness to reuse grey water.
Table 2. Acceptances (as head counts) and changes in attitudes of participants after being informed about grey water reuse

<table>
<thead>
<tr>
<th>Final Option</th>
<th>Before informing</th>
<th>After informing</th>
<th>% increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Household use</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toilet flushing</td>
<td>179</td>
<td>209</td>
<td>17</td>
</tr>
<tr>
<td>Car washing</td>
<td>158</td>
<td>193</td>
<td>22</td>
</tr>
<tr>
<td>Swimming pools</td>
<td>50</td>
<td>81</td>
<td>62</td>
</tr>
<tr>
<td>Irrigation - Agricultural</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cereals/grains</td>
<td>130</td>
<td>161</td>
<td>24</td>
</tr>
<tr>
<td>Nuts in shells</td>
<td>132</td>
<td>175</td>
<td>33</td>
</tr>
<tr>
<td>Fruits on soil</td>
<td>94</td>
<td>135</td>
<td>44</td>
</tr>
<tr>
<td>Fruits on trees</td>
<td>120</td>
<td>157</td>
<td>31</td>
</tr>
<tr>
<td>Cooked vegetables</td>
<td>95</td>
<td>116</td>
<td>22</td>
</tr>
<tr>
<td>Uncooked vegetables</td>
<td>57</td>
<td>93</td>
<td>63</td>
</tr>
<tr>
<td>Irrigation - Landscape</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Home gardens</td>
<td>170</td>
<td>205</td>
<td>21</td>
</tr>
<tr>
<td>Picnic area</td>
<td>159</td>
<td>202</td>
<td>27</td>
</tr>
<tr>
<td>Landscape</td>
<td>162</td>
<td>197</td>
<td>22</td>
</tr>
<tr>
<td>Park</td>
<td>169</td>
<td>204</td>
<td>21</td>
</tr>
<tr>
<td>Stadium</td>
<td>143</td>
<td>183</td>
<td>28</td>
</tr>
<tr>
<td>Playground</td>
<td>166</td>
<td>196</td>
<td>18</td>
</tr>
<tr>
<td>School garden</td>
<td>153</td>
<td>184</td>
<td>20</td>
</tr>
</tbody>
</table>

4. Conclusions
Grey water is a renewable and reliable source of water and can be used as an alternative water source. However, large scale implementation requires positive public opinion and acceptance. In this survey which was undertaken in Istanbul, it was observed that awareness regarding grey water and its reuse was limited and supplying information to raise awareness in the subject matter helped a lot in improving public opinion. The greatest acceptance as the final use was with toilet flushing with 79% acceptance which increased to 92%, the lowest was uncooked vegetables with 25% and increased to 41% after sharing information. Economic considerations were observed to play an important role in public acceptance and approval increased by more than two fold if it is offered for free. Awareness and publicity definitely seems to be a key element in the promotion of this sustainable practice which entails attention by state and local authorities as well as NGOs.

References


Deinking of Waste Office Paper by Chemical Flotation in Recycling

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Keywords: Office papers, Deinking, Flotation,

Abstract

In this study black ink on the laser and inkjet printouts were removed from pulp by applying flotation in paper recycling. Waste office papers were shredded and disintegrated to obtain pulp. Dispersed air flotation system was used to separate ink from the pulp. CaO and NaOH were tried as deinking chemicals by which whiteness value was increased. Recycled paper was produced from deinked pulp and product quality was checked according to Turkish national standards (TSE). Although NaOH was effective, bursting strength and breaking length of the recycled paper reduced when excess NaOH was used in deinking. Considering both deinking performance and chemical cost, CaO was suggested.

1. Introduction

Office paper, packaging paper, cardboard and paper bags have been produced within the scope of paper sector (Official Report, 2012). More than 90% of the produced paper products have been produced from the hard/soft wood pulp (Şahin, 2016; Official Report, 2012). Paper demands tremendously increase all over the world and this has been adversely affecting the ecological balance due to increasing wood utilization (Virk et al, 2013; Şahin, 2013). Increasing environmental sensitivities resulted in preparation of new rules and regulations which encourages and enforces the recycling of waste materials. In Turkey, while 3.745 million tonnes of paper was being produced in 2015, the total paper consumption was 5.865 million tonnes. This means yearly average 57% more consumption requires more paper in the country (SKSV, 2018). This gap has been generally closed by importing paper from abroad. Another solution to this problem is the recovery, recycling of waste paper in the country. It is necessary to encourage this approach by making the recycling culture prevalent.

Paper production from recycled fibres should be encouraged all over the world since recycling conserves natural resources, prevents pollution and consumes less energy. Technologies are available for recycled paper production and use (Bajpai, 2014). Recycled papers are generally brown papers and boards. However, through deinking, white grades can be produced. The techniques used for the production of deinked pulp are completely different than those used for the production of pulp from wood or from other raw material.
The recycling technology is the combination of the various treatments performed to produce a pulp from recovered papers and to clean it. Special treatments are required to remove the ink. Deinking is performed in two steps (Bajpai, 2014). The first step involves ink detachment from the surface of the disintegrated fibres, which is performed during pulping. In the second step, the detached ink particles are removed from the pulp slurry by washing or flotation. Alkaline deinking is being widely used and is considered more efficient for ink detachment than neutral deinking. Therefore, in this study, CaO and NaOH were tried as deinking chemicals to check their deinking performances and resultant recycled paper quality to obtain recycled paper from waste office paper.

2. Materials and Methods

Waste office papers were collected, shredded, soaked into water, disintegrated with a grinder and pulp was prepared. Dispersed air flotation system with 20 L volume was used for deinking. Flotation was applied without chemical, with CaO or with NaOH addition. The scum collected on the surface of flotation system was scrapped. To investigate the effect of chemical dosage, different CaO (10%) or NaOH (10%) dosages were applied at each run. Paper samples were produced from the deinked pulp and the quality of each sample was determined according to Turkish test standards.

3. Results

The quality parameters and their test values for all produced recycled paper samples after deinking process were given in Table 1. Accordingly, % dry matter, Schopper Riegler Freeness number, unit weight, thickness and opacity values of the samples, deinked with or without chemical, were close to each other. Moreover, these values are within the ranges of reference white paper produced from wood-pulp. 0.02-0.05 differences between Dry matter percentages were negligible.

CIE Whiteness value increased from 117.1 to 130 and 129 with CaO and NaOH addition, respectively. Similarly, Iso whiteness and Iso brightness values also increased with chemicals addition in flotation deinking process. These represent the success of deinking procedure. As whiteness get closer to the reference values, that means the recycled paper ink become closer to zero.

Table 1. Comparison of recycled paper properties for different chemical deinking applications

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reference Test Standard</th>
<th>No Chemical</th>
<th>CaO, mg/L</th>
<th>NaOH, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Matter %</td>
<td>TS EN ISO 638</td>
<td>0.27</td>
<td>0.21</td>
<td>0.26</td>
</tr>
<tr>
<td>Schopper Riegler Freeness no</td>
<td>TS EN ISO 5267-1</td>
<td>25</td>
<td>26</td>
<td>25</td>
</tr>
<tr>
<td>Unit weight (g/m²)</td>
<td>TS EN ISO 536</td>
<td>85</td>
<td>75</td>
<td>78</td>
</tr>
<tr>
<td>Thickness (μ)</td>
<td>TS EN ISO 534</td>
<td>146</td>
<td>130</td>
<td>133</td>
</tr>
<tr>
<td>Tearing resistance (% elmendorf)</td>
<td>TS EN ISO 1974</td>
<td>74</td>
<td>64.8</td>
<td>70.2</td>
</tr>
<tr>
<td>Breaking length, km</td>
<td>TS EN ISO 1924-2</td>
<td>3.28</td>
<td>3.05</td>
<td>2.66</td>
</tr>
<tr>
<td>Bursting strength (kgf/cm²)</td>
<td>TS EN ISO 2758</td>
<td>1.23</td>
<td>1.08</td>
<td>1.02</td>
</tr>
<tr>
<td>CIE W D65</td>
<td>TS ISO 117.1</td>
<td>130</td>
<td>126.1</td>
<td>127.1</td>
</tr>
</tbody>
</table>
For low chemical dosage the whiteness levels, the bursting strength and breaking length values of the low dosages were high. Higher dosages of NaOH resulted in significant reductions in bursting strength and breaking length values of recycled papers. Change of properties of recycled papers with applied deinking chemical dosage are compared in Figure 1 where paper quality parameters are grouped at different graphs to observe the effect of chemical on the same group of properties. In Figure 1 the values indicated for each parameter at zero dosage were the value of recycled paper properties without any chemical.
Figure 1. Change of recycled paper quality with deinking chemical dosage. (a) and (b) are paper color parameters, (c) and (d) are paper physical properties, (e) and (f) paper strength properties for CaO and NaOH deinking, respectively.

The most preferable deinking chemical should be the one which results in higher strength and which protects the fibers better (Bhat et al., 1991; Pal et al., 2004). Recycled fibres have lower strength and higher drainage resistance than virgin fibres. This is mainly due to the loss of bonding capacity, which is related to reduced fibre swelling. The reduction in swelling and the loss of fibre flexibility after drying reduces the strength potential of recovered fibres (Bajpai, 2014).

Most of the chemicals used for deinking are standard commodity products. Chemistry plays a role in fibre swelling, ink removal, wetting, anti-re-deposition, dispersion, flocculation,
agglomeration, oxidation and/or reduction of chromophores, etc (Bajpai, 2014). NaOH reduce mechanical strength of the fibers and increase the resistance by affecting the hydrophobicity, and so increasing the water absorption into fibers resulting in softer paper product. Because it helps in fibre swelling, breaks down ink by saponification or hydrolysis and helps in ink dispersion (Bajpai, 2014). Ink collector renders the ink hydrophobicity and facilitates its attachment to the air bubble. Soft paper is not a preferred material for printing purposes etc. A sheet containing recycled fibre is less dense and usually more absorptive than virgin fibre stock. Microfibrils in the pulp behave as fillers, with a small effect on strength but a large effect on the drainage properties. Calcium salts reacts with the collector to form small insoluble calcium soap particles that adhere to the ink particle; calcium helps agglomerate the ink particles into large hydrophobic clusters (Bajpai, 2014). Therefore CaO is a preferable deinking chemical. Moreover, considering the chemical cost, CaO can be suggested as a result of this study.

Conclusion

In order to meet the increasing paper demand without importing raw paper and or pulp, it is essential to encourage paper recycling and recycled paper utilization in the society. As the quality of the recycled paper increase, it becomes easier to society to adopt using it. Paper quality is characterized by its color, its strength and its other physical properties. Waste office papers are generally printouts which contain types of printer inks on the papers. Therefore, in order to have acceptable color in recycled paper, deinking process is applied to the waste paper pulp. Number of types of chemicals available for deinking procedure. Alkali type of chemicals CaO and NaOH were used as deinking chemical in this study. The effects of both chemicals on recycled paper were approximately the same, however, the product quality was better when 100 mg/L CaO was used. CaO is also the cheaper chemical. Although literature on various types of chemicals are available, those studies focused only color of the deinked pulp. However, the recycled sample quality, especially strength shouuld be considered. Therefore, other types of commercially available chemicals especially enzymes and combinations of enzymes with inorganic chemicals should be tried for better quality recycled paper product by considering not only color, but also physical properties and strength.

Acknowledgement

The authors would like to acknowledge Kombassan A.S. Paper Factory for their support in experimental part of this study.

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Treatment of Microplastics

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Keywords: Microplastic, wastewater, treatment, microbead, microlitter

Abstract

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

1. Introduction

Microplastics particles (MPs) are new anthropogenic pollutants found in different aquatic environments, including oceans, rivers, lakes and estuaries, as well as at the effluent of urban sewage and wastewater (Eerkes-Medrano et al., 2015). MPs are plastics smaller than 5 mm (Van Cauwenberghe et al., 2015). They can be categorized into primary MPs and secondary MPs. Primary MPs are manufactured to have a size less than 5 mm and mainly found in textiles, medicines and such personal care products as facial and body scrubs (Cole et al., 2011; Browne, 2015). Secondary MPs are resulted from the decomposition of larger plastics due to such processes as photo-degradation, physical, chemical and biological interactions.

All plastics types may cause adverse effects on organisms and ecosystems. (Van Cauwenberghe et al., 2015). Cosmetic products may contain between 0.5 and 5% of microbeads known as primary MPs. Microbeads have an average size of 250 μm (GESAMP, 2010; Zikto and Hanlon, 1991). Also, they find toothpaste and remove plaque and stains due to their abrasive action. Toothpaste releases around 4000 and an exfoliant wash can release 4500–94,500 microbeads with one time use (Carr et al., 2016; Napper et al., 2015). MPs like these are can be transported by rivers, discharge from water treatment plants, wind and surface run-off into either fresh water and seawater environments and fishing nets, industrial resin pellets, household items and other discarded plastic debris (Gall and Thompson, 2015; Eerkes-Medrano et al., 2015). MPs may become more dangerous by adsorbing harmful agents such as pharmaceuticals and pathogenic organisms (McCormick et al., 2014; Ziajahromi et al., 2017).

MPs are more abundant in wastewater. Municipal wastewater treatment plants (WWTPs) are typically designed based upon a common schematic though each facility will differ slightly. Primary and secondary treatment processes of their can remove MPs from the wastewater up to 99% and most of the MPs are removed already during pretreatment phases (Carr et al., 2016; Murphy et al., 2016; Talvitie et al., 2017). In some published reports (McCormick et al., 2014, Browne et al., 2011), WWTPs were mentioned as potential
sources of MPs in aquatic systems. Despite the efficacy of removal, most studies still noted MP counts within the effluent stream (Magnusson and Wahlberg, 2014; Martin and Eizhvertina, 2014; Carr et al., 2016; Murphy et al., 2016). The aim of this study was reviewed to investigate the efficiency of their and used methods to remove MPs from wastewater.

2. Materials and Methods

The MPs and fibers from both water and sludge samples can be identified either using more reliable identification analyses or visually (Andrady, 2011; Hidalgo-Ruz et al., 2012). They generally determined Fourier transform infrared spectroscopy (FTIR) or Raman spectroscopy (Browne et al., 2011; Murphy et al., 2016; Talvitie et al., 2017a; Ziajahromi et al., 2017). Some researchers are based on a visual identification only (Mason et al., 2016; Michielssen et al., 2016; Talvitie et al., 2015). However, MPs have relied on a combined methodology of identification by defining possible MPs visually and then analyzing only part of them (Carr et al., 2016; Magnusson and Noren, 2014; Mintenig et al., 2017).

3. Results

WWTPs can remove MPs from the wastewater. They can act as a barrier. Primary and secondary treatment processes in WWTPs are obtained removal efficiency 99%. However, WWTPs suggested as significant point source of MPs pollution. Carr et al. investigated these suspicions (Carr et al. 2016). They evaluated MPs treatment effluent discharges from seven tertiary plants and one secondary plant in Southern California. According to the results, they proposed that MPs are effectively removed with the stripping and settling treatment processes and so tertiary effluent is not a major source of MPs. Also, primary treatment process such as solids stripping and sludge settling MPs were found to be removed mostly and existing treatment processes were determined to be very effective for removal of MPs pollution.

Talvitie et al. have done the most comprehensive research about treatment of MP (Talvitie et al. 2017b). They investigated the removal of MPs utilizing different advanced final-stage treatment technologies. Membrane bioreactor (MBR) was included primary effluent in WWPTs and different tertiary treatment technologies (discfilter, rapid sand filtration and dissolved air flotation) were used to treating secondary effluent in WWPT. As a result, the MBR gave also the lowest MPs concentration among using tertiary treatment technologies in the final effluent. Removal efficiency of MPs was obtained rapid sand filter removed 97%, dissolved air flotation 95% and discfilter 98.5% MBR 99.9%.
Figure 1. Microplastics derived from personal care products (Talvitie et al, 2017)

Also Talvitie et al. studied treatment of microlitter from wastewater during different treatment steps in advanced WWTPs (Talvitie et al., 2017a). These steps contain mechanical, chemical and biological treatment and biologically active filter. According to the results of the study, Pre-treatment and activated sludge treatment removed almost 97% of the microlitter. Activated sludge process contributed to decrease the microlitter concentration and pretreatment greatly affect positively on microlitter size distribution. After secondary treatment, the overall retention capacity WWTPs was achieved over 99%.

Peren et al. investigated treatment with electrocoagulation of MPs. In this study was used artificial wastewater containing polyethylene microbeads of different concentrations. Microbead removal efficiencies in excess of 90% were observed in all experiments. However, the optimum removal efficiency was 99.24% pH=7.5. The results showed that EC is an effective method of removing MPs contaminants from wastewater streams (Peren et al., 2018).

It is noted that there is no much study about treatment of MPs in the literature. This is required to be investigated. Because present WWPTs effluents still contain MPs. Mason et al. investigated WWPTs effluent. For this, 17 different facilities in the United States were taken ninety samples and analyzed. 0.05 ± 0.024 MPs were found per liter of effluent on the average all facilities (Mason et al., 2016). These results showed that WWPTs are releasing over 4 million MPs per facility per day.

Lares et al. investigated the efficiency of a municipal WWTP to remove MPs from wastewater. Wastewater and sludge samples were analyzed. MPs removal efficiency was found to be 98.3% in studied WWTP. Also, this study showed that before the activated sludge process, MPs was removed. However, they stated MPs are discharged from the WWTP to the aquatic environment.

4. Conclusions

This paper, literature researches have been prepared to reviewed. It is seen that the water ecosystem on the world is under serious danger in terms of MPs. The biggest source of this is WWPT. According to most research, treatment of MPs by WWTPs have affected however WWTPs were mentioned as potential sources of MPs in aquatic systems. For this, WWPT
should be designed to remove MPs. Advanced treatment technologies and more research is needed.

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Inhibition Effect of Different TiO$_2$ Nanoparticles on the Oxygen Uptake Rate (OUR) of Activated Sludge Microorganisms

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

Abstract

TiO$_2$ nanoparticles (NPs) are the most studied ones to develop self-cleaning and antibacterial nano textiles. However, the negative effects of NPs and the risk of possible release of NPs into the wastewater process and then aquatic environment are not well known yet. Oxygen uptake rate (OUR) measurements have been realized as more reliable methods compared to instant determination of the OUR response of the activated sludge systems for toxicity and inhibition studies. Activated sludge inhibition tests of NPs applied synthetic wastewater samples, were conducted in accordance with a test procedure described by ISO 8192. Activated sludge was acclimated in lab-scale Fill and Draw Reactors (F&DRs). The EC$_{50}$ level as defined by ISO 8192 after 30 min and 180 min of reaction time for TiO$_2$ NPs was calculated and corresponds to 1654 mg/L and 1670 mg/L for Ti, respectively. EC$_{50}$ values of 3% Ag added to TiO$_2$ NPs sol-gel and 2% Cu added to TiO$_2$ NPs sol-gel were calculated to be 147 mg/L and 166 mg/L, 620 mg/L and 386 mg/L respectively after 30 min and 180 min of exposure times.

1. Introduction

Nanotechnologies are focused on the creation or manipulation of nanometric dimension particles and materials, (from 1 to 100 nm). Face to the growing industrial use of nanomaterials, NPs are expected in aquatic and terrestrial environments (Clement et al., 2013). TiO$_2$ is among the most frequently reported engineered materials used in nanotechnology-based consumer products that have been used for decades (Kiser et al., 2009). Nanotechnology is one of the most promising interdisciplinary technologies that have been spreading different sectors and becomes very indispensable for human life. In addition to these applications, in the recent years, it has been very common in environmental projects (Qian and Hinestroza 2004). Nanotechnologies/Nano-devices which remove water, air and soil pollution as an alternative treatment method, and products which cause less waste and pollution and need fewer raw materials during manufacturing are main applications of nanotechnology in environmental sector. TiO$_2$ NPs are widely applied in catalysts, sunscreens, cosmetics, paints, plastics and wastewater treatment processes. The occurrence of TiO$_2$ NPs in the environment has recently aroused public attentions regarding their potential effects on the biota and human health (Li et al., 2017). Application of nanotechnology in the textile products is still very early in its infancy but it is already proving to be a useful tool in improving the performance of textiles. TiO$_2$ NPs are the most studied NPs in the cotton textile industry to develop self-cleaning and anti-bacterial cotton products (Gupta et al., 2007).
Respirometry has been used very efficiently for identifying and understanding the biochemical mechanisms involved in the activated sludge process. On-line oxygen uptake rate (OUR) measurements have been realized as more reliable methods compared to instant determination of the OUR response of the activated sludge systems for toxicity and inhibition studies (Karahan, 2010). A number of successful applications of respirometry have been reported which have been used to understand and predict different biochemical mechanisms of activated sludge systems (Meriç et al., 2003; Karahan, 2010; Çalhan, 2012).

This study aims to investigate inhibition effects imposed by sol-gel based TiO₂ NPs of activated sludge system using OUR. In this context, this study will provide a better understanding of the inhibition mechanisms and the results of the study will be useful in the solution of operational problems of activated sludge systems.

2. Materials and Methods

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

![Experimental set-up](image)

**Figure 1.** Experimental set-up

2.1 Activated sludge inhibition tests

OUR measurements have been realized as more reliable methods compared to instant determination of the OUR response of the activated sludge systems for toxicity and inhibition studies. The aim of this study is to investigate inhibition effects imposed by sol-gel based TiO₂ NPs of activated sludge system using OUR. Activated sludge inhibition tests of NPs applied synthetic wastewater samples, were conducted in accordance with a test procedure described by ISO 8192 (ISO 8192, 2007). The experimental setup has been prepared with the acclimation of activated sludge taken from a municipal wastewater...
treatment plant in Denizli, Turkey. Activated sludge was acclimated in two lab-scale F&DRs, which had a working volume of 2 L. The reactors had hydraulic retention time of 1 day and it was fed with synthetic sewage representing domestic wastewater at fixed F/M ratio of 0.3 mg COD per mg VSS per day. 16 g peptone, 11 g meat extract, 3 g urea, 0.7 g NaCl, 0.4 g CaCl₂·H₂O, 0.2 g MgSO₄·7H₂O, and 2.8 g K₂HPO₄ were dissolved in 1 L of distilled water to prepare synthetic sewage stock solution. Each nitrification inhibitor, Formula 2533™ was added to the reactors at a concentration of 0.16 g for 300 mL volume. The reactors were aerated so that the dissolved oxygen levels were above 5 mg/L, pH was checked periodically and it was always between 6.5 to 7.5 during the experiments. Dissolved oxygen measurements were performed by a WTW Inolab OXI 740 model oxygen meter in 50 mL air-tight vessels. Repeated experiments were performed by using TiO₂ NPs, prepared with sol-gel method, for periods of 30 to 180 min.

3. Results

The respirometric assessment of the inhibitory impact of TiO₂ NPs and TiO₂ NPs with metal doped which has the best self-cleaning and anti-bacterial properties on substrate utilization by activated sludge has been performed with the synthetic sewage (peptone-meat extract) as described with the standard procedure (ISO 8192, 2007). The ISO procedure requires running a set of aerated batch reactors with a range of inhibitor concentrations, using the synthetic sewage and biomass previously acclimated to the substrate adjusted to fixed an initial food to microorganism (F/M) ratio of 0.3 mg COD per mg VSS per day. The EC₅₀ level as defined by ISO 8192 after 30 min and 180 min of reaction time for TiO₂ NPs was calculated and corresponds to 1654 mg/L and 1670 mg/L for Ti, respectively (Figure 2 and Figure 3).

![Figure 2. Results of the EC50 test for TiO₂ NPs sol-gel after 30 min](image)

![Figure 3. Results of the EC50 test for TiO₂ NPs sol-gel after 30 min](image)

In the activated sludge system on the microorganisms more evident inhibition effect was observed when TiO₂ NPs were doped with copper (2% Cu added to TiO₂ NPs sol-gel) as EC₅₀ values were calculated as to be 620 mg/L and 386 mg/L after 30 and 180 min of exposure times respectively. However, silver has more inhibition effect on the microorganisms than copper added solution in lower concentrations. As a result of 30 and 180 minutes reaction time of 3% Ag added NPs EC₅₀ values were obtained as 147 mg/L and 166 mg/L, respectively. As seen that in the Figure 4-Figure 7, the experimental data indicate that a good logarithmic correlation between the inhibitor concentration and percent decrease in the corresponding OUR level for the range of TiO₂ NPs concentrations tested in the study.
4. Conclusion

In this study, it is investigated that the toxicity effect on the microorganism in the activated sludge, of the NPs which are emerged by being used in nano technological coatings, to give the features to the fabric in the textile industry. TiO$_2$ NPs and two metal doped TiO$_2$ NPs were selected and applied, in this study. By monitoring the OUR of the activated sludge the effects of biological treatment system is investigated. The titanium (Ti) concentration was found as EC$_{50}$ inhibition concentration at the point of 50% of OUR was blocked.

The EC$_{50}$ level after 30 min and 180 min of reaction time for TiO$_2$ NPs was calculated and corresponds to 1654 mg/L and 1670 mg/L for Ti. TiO$_2$ NPs with metal doped which has the best anti-bacterial and self-cleaning properties after 30 min and 180 min of reaction time, EC$_{50}$ values of 147 mg/L and 166 mg/L, 620 mg/L and 386 mg/L were obtained as a result. Silver which is known to have anti-bacterial properties has more inhibition effect on the microorganisms than copper added solution in lower concentrations.

It is thought to get more realistic results in the case of the study is carried out with the textile wastewater in the biological treatment system, TiO$_2$ particles mixed with activated sludge and treated water have been found that only very small concentrations because of the

Figure 4. Results of the EC$_{50}$ test for TiO$_2$ NPs with Ag (3%) doped after 30 min

Figure 5. Results of the EC$_{50}$ test for TiO$_2$ NPs with Ag (3%) doped after 180 min

Figure 6. Results of the EC$_{50}$ test for TiO$_2$ NPs with Cu (2%) doped after 30 min

Figure 7. Results of the EC$_{50}$ test for TiO$_2$ NPs with Cu (2%) doped after 180 min
adsorption and precipitated on activated sludge. It is expected that this study can contribute to ongoing and future studies to understand the TiO\textsubscript{2} NPs inhibition effect on the activated sludge system.

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Use of Nano Zero-Valent Iron Coated Coffee Grounds Composite for Removal of Zinc and Nickel from Model Electroplating Waste Water

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Abstract

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

1. Introduction

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

2. Materials and Methods

2.1. Materials and Chemicals

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

2.2. Preparation of nZVI Particles

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

2.3. Characterization studies

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

2.4. Removal of Nickel and Zinc

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

3. Results

3.1. Characterization of CG and CG-nZVI

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

![Figure 1. SEM images of CG (left) and CG-nZVI (right).](image)

3.2. Effect of pH on Ni and Zn removal

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

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

References


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