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Electrocoagulation of tissue paper wastewater and an evaluation of sludge for pyrolysis

Umran Tezcan Un[a,*], Seher Topal[b], Funda Ates[c]

[a]*Faculty of Engineering, Department of Environmental Engineering, Anadolu University, Iki Eylul Campus, 26555 Eskisehir, Turkey, Tel. +90 222 321 35 50, ext. 6418; email: utezcan@anadolu.edu.tr*
[b]*Graduate School of Sciences, Anadolu University, Yunusemre Campus, 26555 Eskisehir, Turkey, email: seher.topal@gmail.com*
[c]*Department of Chemical Engineering, Anadolu University, Iki Eylul Campus, 26555 Eskisehir, Turkey, Tel. +90 222 321 35 50, ext. 6342; email: fdivrikl@anadolu.edu.tr*

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ABSTRACT

In this study, the electrocoagulation (EC) of tissue paper wastewater is studied using iron and aluminum flat blade disk turbine-type anodes and a cylindrical iron cathode. The effect of several parameters, such as supporting electrolyte concentration, current density, pH, agitation speed, H_2O_2 concentration, and type of electrode material on chemical oxygen demand (COD) removal efficiency, is determined. It can be seen that except for agitation speed, all remaining parameters have a positive effect on COD removal. The best treatment efficiency is observed at the original pH of the wastewater (pH 7.4) with an initial COD of 1,220 mg/L, reduced to 90 mg/L, resulting in an overall removal efficiency of 92.6%. In addition, the sludge is evaluated as a catalyst in a fast pyrolysis process. It is found that when the sludge is used as a catalyst in the pyrolysis process, the quality of the bio-oil product improved.

Keywords: Tissue paper wastewater; Electrocoagulation; Sludge; Catalyst; Pyrolysis

1. Introduction

The pulp and paper industry has grown rapidly over the last decade, consuming large volumes of water [1]. The tissue paper industry, which has grown in proportion to increasing urbanization, needs greater attention. The wastewater from this industry in general has a high chemical oxygen demand (COD), insoluble organic material, biological oxygen demand, color, and total suspended solids [2]. One of the main unwanted constituents in this wastewater is lignin, which resists traditional biological treatment due to its complex chemical structure. The wastewater must be treated before being discharged into municipal drainage systems to comply with regulations.

Several processes, such as chemical precipitation, activated sludge, and anaerobic treatment, have been used for the treatment of paper wastewater. Of these, electrocoagulation is the preferred technique. Little has been reported in the literature regarding the treatment of tissue paper wastewater [3,4]. The main drawback of electrocoagulation research for paper waste water is the use of similar types of electrode, in particular parallel plate configuration. Electrocoagulation of paper mill effluent has been performed using aluminum and iron plate anodes by Ugurlu et al. [5],

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*Corresponding author.

using six parallel plate electrodes by Zaied and Bellakhal [6], using eight parallel plate electrodes by Katal and Pahlavanzadeh [7], using two aluminum and iron electrodes by Zodi et al. [8], using four iron monopolar electrodes by Vepsäläinen et al. [9], and using single and four aluminum plate electrodes by Terrazas et al. [4].

Electrocoagulation as an evolving technology can be applied effectively for the treatment of various wastewater, such as metal plating wastewater [10], baker's yeast wastewater [11], and municipal wastewater [12]. During electrocoagulation, when a potential difference is applied between a soluble Fe anode and a cathode, ferrous ions form at the anode followed by *in situ* oxidation to the ferric state (Eqs. (1) and (2)) and hydroxyl ions are then generated at the cathode (Eq. (3)). Then, hydroxides precipitate with ferric ions as ferric hydroxide (Eqs. (4)–(6)) which are responsible for the effects observed during particle aggregation. The reactions are as follows [13,14]:

Anode:

$$4Fe_{(s)} \rightarrow 4Fe^{2+} + 8e^{-} \tag{1}$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-} \tag{2}$$

Cathode:

$$2H_2O + 2e^{-} \rightarrow H_{2(g)} + 2OH^{-} \tag{3}$$

In the solution (with dissolved oxygen):

$$4Fe^{2+} + O_{2(g)} + 10H_2O \rightarrow 4Fe(OH)_{3(s)} + 8H^{+} \tag{4}$$

$$Fe^{3+} + 3OH^{-} \rightarrow Fe(OH)_{3(s)} \tag{5}$$

$$Fe^{2+} + 3OH^{-} \rightarrow FeOOH_{(s)} + H_2O + e^{-} \tag{6}$$

However, one inherent disadvantage of electrocoagulation is the generation of large quantities of waste sludge that needs further treatment and correct disposal. In the literature, few studies have focused on sludge generated during electrocoagulation. Generally, the settling characteristics of electrocoagulated sludge were determined by Zodi et al. [15], by Ricordel and Djelal [16], and by Lai and Lin [17]. The dehydration of electrocoagulated sludge [18] and the anaerobic stabilization of sludge [19] have also been studied. There have been few studies which have focused on the electrocoagulation of sludge regarding waste utilization. Sludge has been used as an adsorbent in the removal of textile dye [20] and used as a raw material in the production of ceramic pigments, to reduce the environmental effects of the sludge and the pigment [21].

In this study, the treatment of tissue paper wastewater was studied by electrocoagulation. As seen from electrocoagulation studies in the literature, parallel plate electrodes are the most popular electrode type used for the treatment of various wastewater. In this study, a uniquely designed iron flat blade disk turbine-type anode is developed, which to date has not been encountered for electrocoagulation in the literature. The effect of several parameters, such as supporting electrolyte concentration (0.03, 0.05, 0.1 M Na_2SO_4), current density (5, 10, 20, 30 mA/cm^2), pH (3, 5, 7.4, 9), agitation speed (50, 100, 150 ppm), H_2O_2 concentration (0.05, 0.1, 0.2), and electrode material (iron and aluminum), was determined. In addition, the sludge produced during the electrocoagulation process was evaluated in the pyrolysis process as a catalyst, a procedure not previously encountered in the literature. There have been few studies which have focused on electrocoagulation of sludge regarding waste utilization.

2. Using electrocoagulation sludge as a catalyst in the pyrolysis process

In general, the iron or aluminum electrodes used in the electrocoagulation process generate $Fe^{3+}_{(aq)}$ or $Al^{3+}_{(aq)}$ ions, which immediately undergo further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides. The sludge resulting from this process thus contains metal oxides which can be a potential resource in numerous applications.

Iron oxide-based materials are commonly used as catalyst in numerous applications. Due to the metallic state of iron, they are found to have good tar cracking properties [22]. Their catalytic activity is found to be high in nanoparticle form, which generally results in high BET surface area containing more coordinated unsaturated sites [23].

The sludge, evaluated as a catalyst in this study, is a complex mixture of mostly ferric oxide, and other minor compounds, such as aluminum oxide, magnesium oxide, silicon oxide, and calcium oxide. When evaluating its content, it can be compared to the red mud which is the solid residue from the Bayer process. It mainly contains Fe_2O_3, Al_2O_3, SiO_2, TiO_2, Na_2O, and CaO.

In the literature, several authors have evaluated iron-based materials or red mud as a catalyst and compared their catalytic activity with other catalysts during pyrolysis or gasification.

Khelfa et al. [24] studied the steam gasification of Miscanthus Giganteus using hematite (Fe_2O_3), a versatile catalyst, at 850°C. In this process, the content of aliphatic ketones, furan derivatives, alkyl phenols, and phenol decreased, while oxyphenols, diols, and aromatics increased. Akalin and Karagoz [25] also used Fe_2O_3 as catalyst along with $SnCl_4$, Al_2O_3, and $AlCl_3$ in the pyrolysis at 500˚C. In their study, the content of alkanes, phenols, carbonyl groups, and benzene derivatives increased, while N-containing compounds, acids and esters, and PAHs decreased. In addition, they found that Fe_2O_3 has more cracking ability than other catalysts. Shao et al. [26] studied the catalytic effect of metal oxides (CaO, Fe_2O_3, Al_2O_3, TiO_2, and ZnO) on the pyrolysis of sewage sludge and found accelerated initial decomposition of sludge due to these catalysts.

Duman et al. [27] and Dulger Irdem et al. [28] used red mud as a catalyst in their gasification experiments. It was found to be active on tar reformation. In another study, red mud was used as a catalyst for the upgrading of hempseed pyrolysis bio-oil [29]. The bio-oil was upgraded by red mud, and it was found to contain fewer carbonyl-containing and oxygenated compounds and more saturated hydrocarbons when compared to a non-catalytic procedure. The researchers found that red mud has catalytic activity for deoxygenation and cracking reactions. Red mud converted carbonyl groups and carboxylic acids to less reactive deoxygenated products. Yathavan and Agblevor [30] studied the catalytic pyrolysis of pinyon-jumper (475˚C) using red mud. They found that aliphatics and aromatics increased, while methoxy compounds, carboxylic acids, and carbonyl groups decreased in comparison with non-catalytic pyrolytic oils. Furthermore, fast pyrolysis of poplar wood using MgO, CaO, TiO_2, Fe_2O_3, NiO, and ZnO was carried out using analytical Py-GC/MS [31]. It was found that Fe_2O_3 effectively increased the formation of various hydrocarbons and aromatics when compared with others.

3. Materials and methods

3.1. Electrocoagulation of tissue wastewater

3.1.1. Wastewater

The wastewater samples were collected from a tissue paper company, located in Izmit, Turkey. The samples were collected from a line at the entrance to the wastewater treatment plant. The initial COD concentration of the wastewater was 1,220 mg/L, and the pH was 7.4. When required, a pH adjustment was conducted using 0.1 M H_2SO_4 and/or 0.1 M NaOH. In this work, an analytical grade reagent was used without further purification.

3.1.2. Electrocoagulation reactor and experimental procedure

Experiments were carried out in a batch electrochemical iron cell, 10 cm in height, with a diameter of 8.2 cm. The iron cylindrical reactor acted as a cathode. An iron flat blade disk turbine-type stirrer with eight blades (each blade measuring 1.8 cm × 3 cm) was used during the electrocoagulation to maintain gentle agitation. The stirrer uniformly distributed the dissolved iron through the mass of wastewater, thereby aiding the formation of flocs. In addition, an iron flat blade disk turbine-type stirrer was also used as a sacrificial electrode. The iron disk turbine-type stirrer, different from the traditional type, was used as an anode, and the reactor tank was used as a cathode for electrocoagulation.

The setup of the laboratory scale batch electrocoagulation (EC) system is shown in Fig. 1. In each experiment, 500 ml of wastewater was poured into the reactor, the pH was then adjusted to the desired value, and Na_2SO_4 was added as a supporting electrolyte to increase conductivity. Then, the disk turbine anode, mounted as a mechanical stirrer head, was immersed into the cathode compartment containing the wastewater and set to agitate the wastewater. Next, current was applied to the anode and cathode by a power supply (Statron, Type 2257). The pH, voltage, temperature, and conductivity were monitored during electrocoagulation, but not controlled. Samples were taken every 15 min and filtered before analysis for residual COD. Determination of the COD concentration was performed after the digestion of a sample in a Hach COD Digester using the titrimetric method. All the analyses were repeated twice for accuracy.

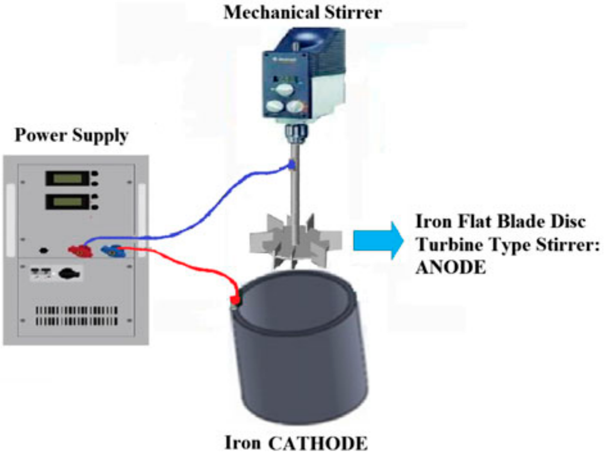

Fig. 1. Experimental setup.

3.1.3. Electrical energy consumption

Electrical energy consumption (EEC) is essential for an evaluation of the cost of electrocoagulation. It was calculated as kWh/m^3 using Eq. (7), where EEC is the electrical energy consumption (kWh/m^3), I is the current (A), t is time (h), U is the potential (V), and V is the volume of the treated solution (m^3):

$$\mathrm{EEC}\left(\frac{\mathrm{kWh}}{\mathrm{m}^3}\right) = \frac{UIt}{V} \times 10^{-3} \tag{7}$$

3.2. Evaluation of sludge as a catalyst in pyrolysis

3.2.1. Preparing the biomass sample and catalyst

In this study, canola seed press cake, supplied from a local company, was used as a biomass sample. The canola samples were ground and screened to give a $0.425 < D_p < 0.85$ mm particle size. Residual sludge from the electrocoagulation of tissue paper industry wastewater was calcinated at 450°C for six hours to activate it. It was then evaluated as a potential catalyst for the pyrolysis experiments.

3.2.2. Experimental pyrolysis setup

The pyrolysis experiments were carried out at a pyrolysis temperature of 500°C in a fixed bed reactor, 90 cm in length, with an inner diameter of 8 mm. Three grams of raw material was used for each experiment. The experiments, using activated sludge as a catalyst (0, 5, and 10 wt%), were performed using an ex-bed mode. Firstly, the activated sludge was placed toward the bottom of the reactor, with the biomass being placed above it. The sludge and biomass sample were fixed using steel wool. Pressure was provided by nitrogen gas during the pressurized pyrolysis experiments. A detailed description of the pressurized experimental procedure can be found elsewhere [32]. The retention time was three minutes during the pressurized pyrolysis experiments.

3.2.3. Characterization of bio-oil and sludge as a catalyst

A Hewlett-Packard HP 7890 gas chromatograph, coupled to a HP 5975 quadruple detector (GC/MS), was used for the bio-oil analysis. The gas chromatograph was equipped with a 30 m × 0.25 mm capillary column coated with a 0.25-μm-thick film of 5% phenyl-methylpolysiloxane (HP-5). The carrier gas was helium. A detailed description of this method can be found elsewhere [32].

After the electrocoagulation experiment, the bulk was settled for 24 h. The waste sludge was then separated from the treated wastewater and dried until in a drying oven (Nuve Model No: FN 120) at 100°C for 24 h, until no moisture remained. The chemical composition and the phases of the sludge were determined using an X-ray fluorescence spectrometer (XRF) (RIGAKU, Rix 2000) and an X-ray diffractometer (XRD) (RIGAKU, D/Max-IIIC) with an Ni-filter, and Cu Kα radiation with a goniometer speed of 1°/s. The XRF analysis shows that the sludge was composed of the following compounds (wt%): Fe_2O_3 (80.12); Al_2O_3 (0.19); MnO (0.38); SiO_2 (0.59); and CaO (0.91). From Fig. 2, obtained from the XRD, it can be seen that the Fe_2O_3 is in the form of maghemite.

4. Result and discussion of electrocoagulation of tissue paper wastewater

4.1. Effect of the supporting electrolyte concentration

The underlying phenomena of electrocoagulation processes are the heterogeneous ion transfer reactions which are affected by the conductivity of the solution. The solution conductivity plays a significant role in current efficiency, as well as the voltage of the system, and hence, EEC. Generally, a supporting electrolyte is added to the wastewater to increase solution conductivity and to reduce the EEC of the electrocoagulation. Na_2SO_4 was used as a supporting electrolyte in this study, and the effect of its concentration on the efficiency of the COD removal and the EEC of the EC process were also studied at a current density of 10 mA/cm^2 and a pH of 7.4 (original pH of the wastewater). As can be seen from Fig. 3, an increase in Na_2SO_4 concentration from 0 to 0.03 M results in an increase in removal efficiency, from 53 to 75%. This suggests that the presence of Na_2SO_4 improves ion movement. However, further improvement in removal efficiency is not observed when the supporting electrolyte concentration is increased to 0.1 M, which may be due to an increase of the passivation layer. The presence of the supporting electrolyte also reduces the EEC, as shown in Fig. 4. This may be due to the increase in the electrical conductivity values correspondingly from 5, 6.5, 8, 12.6 mS/cm, in proportion to molar concentrations of electrolyte of 0, 0.03, 0.05, and 0.01 M. An EEC of 178 kWh/m^3 was reduced to 15 kWh/m^3 using 0.1 M Na_2SO_4. Consequently, a value of 0.03 M concentration of the supporting electrolyte was chosen to obtain high removal efficiency, as well as to reduce EEC. The EEC of the reactor was also dependent on time. The EEC linearly increases from 2.3 to 15 kWh/m^3 wastewater

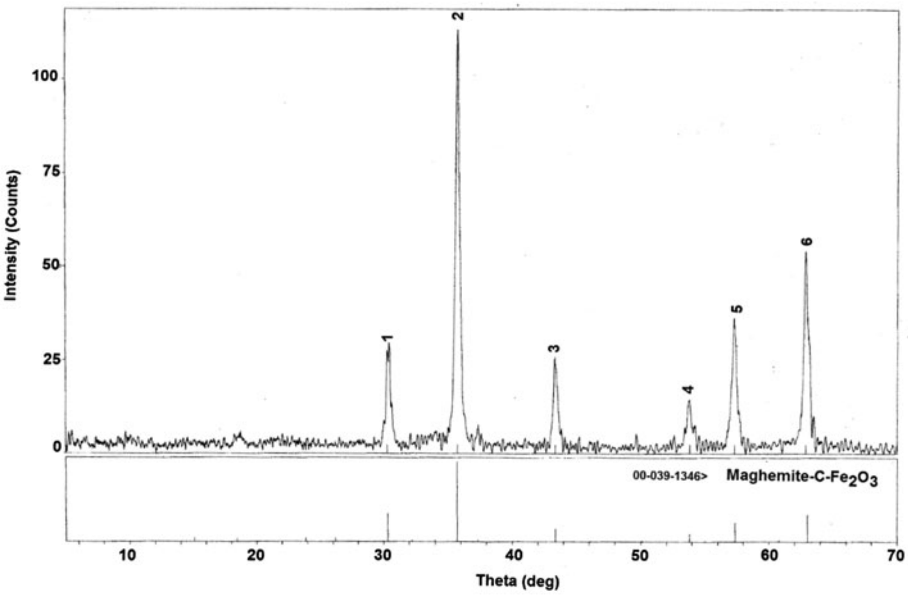

Fig. 2. XRD pattern of the sludge.

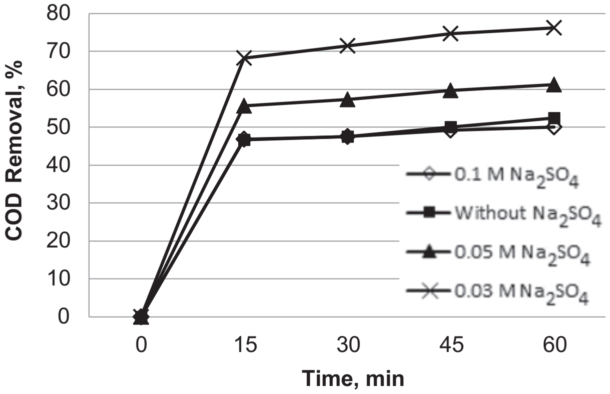

Fig. 3. The effect of Na_2SO_4 concentration on the COD removal. *i*: 10 mA/cm^2, pH 7.4, agitation speed: 100 rpm.

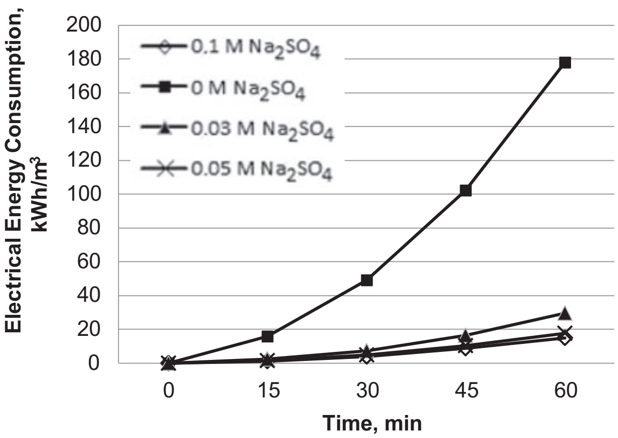

Fig. 4. The effect of Na_2SO_4 concentration on EEC. *i*: 10 mA/cm^2, pH 7.4, agitation speed: 100 rpm.

with an increasing reaction time from 15 to 60 min at 10 mA/cm^2, 0.1 M Na_2SO_4. In addition, a maximum COD removal of 48% was achieved after 15 min, while COD removal at 60 min was 50%. The EEC at 60 min was 6.5 times higher than that for 15 min. A similar result was obtained for 0.03 M Na_2SO_4. A removal efficiency of 68% was obtained at 15 min using 3 kWh/m^3 EEC, while a 76% removal efficiency was obtained using 29 kWh/m^3 EEC. Thus, an optimum operational time and conditions should be determined according to the desired effluent quality and the cost of EEC.

4.2. Effect of current density

Current density is defined as the current applied per unit of electrode area. It is an important parameter which determines the coagulant dosage rate in electrocoagulation performance. The effect of current density was studied at 0.03 M Na_2SO_4 and a pH of 7.4. A significant increase in removal efficiency was observed within 15 min for all current densities. The amount of dissolved iron hydroxides increased over time, and also resulted in an increase in floc formation. After 60 min of electrolysis, removal efficiencies of 65, 75, 80, and 84% were obtained at current densities of 5, 10, 20, and 30 mA/cm^2, respectively, as shown in Fig. 5. It can also be observed that the process with 30 mA/cm^2 consumed the least amount of energy, 11.5 kWh/m^3, when compared with energy consumption of 31 and 21 kWh/m^3, at current densities of 10 and 20 mA/cm^2, respectively, for the same removal efficiency of 75%. This is due to the decrease in time taken for the processes to attain this removal efficiency, which was observed as 60, 30, and 15 min for current densities of 10, 20, and 30 mA/cm^2.

In general, the amount of dissolved iron will increase in proportion to current densities, which can result in higher removal efficiency, but also with a proportional increase in EEC (Fig. 6). Therefore, selection of an optimum current density, which gives high removal efficiency with relatively low EEC, is necessary. However, in our study, in order to obtain direct dischargeable effluents, the experiments were performed at 30 mA/cm^2, which gave a 75% removal with an EEC of 11.5 kWh/m^3 within 15 min. These results are comparable with values published by other groups in the literature. Sridhar et al. [33] found an EEC of 10.1–12.9 kWh/m^3 for a 90% reduction in COD of pulp and paper industry bleaching effluent with an initial COD concentration of 600 mg/L. Fajardo et al. [34] found an electrical consumption of 34 kWh/m^3 for 40.3% reduction in initial COD of 1,118 mg/L of phenolic wastewater treatment. Ilhan et al. [35] found an EEC of 39.7 kWh/m^3 to achieve a 59% reduction in COD of leachate wastewater, with an initial value of 12,860 mg/L.

As can be seen from the results, to reach a certain removal efficiency, electrocoagulation time is one of the main parameters that affects the performance of the reactor as well as EEC.

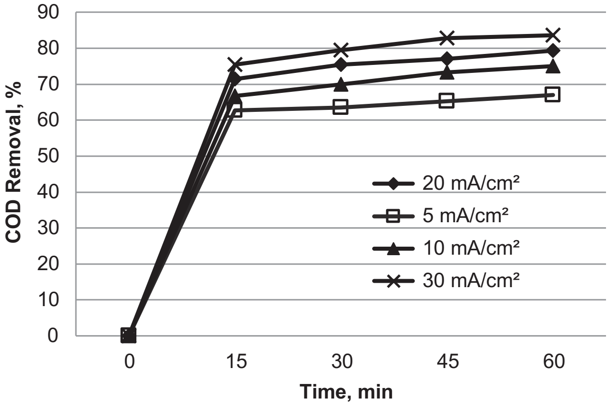

Fig. 5. The effect of current density on COD removal. pH 7.4, Na_2SO_4: 0.03 M, agitation speed: 100 rpm.

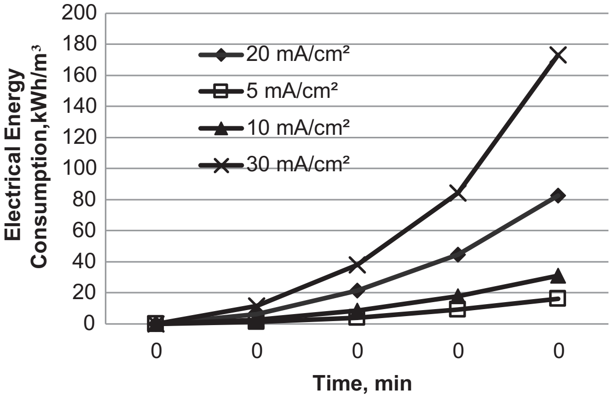

Fig. 6. The effect of current density on EEC. pH 7.4, Na_2SO_4: 0.03 M, agitation speed: 100 rpm.

4.3. Effect of initial pH

In the electrocoagulation process, complicated reactions depend on solution pH. The pH of the solution determines the intermediates and the pathway of the reaction. In the current study, the effect of pH was determined at a current density of 30 mA/cm^2 and 0.03 M Na_2SO_4. The results can be seen in Fig. 7. Removal efficiencies were found to increase by increasing the pH from 3 to 7.4. A further increase of pH to 9 had an adverse effect on removal efficiency. The best removal efficiency was obtained at a pH of 7.4 (original pH of the wastewater). Lower removal efficiencies were obtained when the initial pH deviated from 7.4. A similar result was obtained by Fouad [36].

4.4. Effect of agitation speed

In the electrocoagulation process, metal hydroxides stabilize dispersed particles. Thus, electrostatic repulsion between the particles will reduce. Agitation speed plays an important role in bringing particles closer together, to a point where van der Waal's attraction becomes predominant and also provides the uniform bulk distribution of generated ions [37]. Although a high agitation speed will create a good opportunity for particles to get closer, it can also lead to the breakup of resulting flocs. Therefore, an optimum agitation speed should be evaluated. In the current study, the effect of agitation speed was determined at conditions of 30 mA/cm^2, pH 7.4, and 0.03 M Na_2SO_4. As can be seen from Fig. 8, removal efficiency decreased with an increased agitation speed. A removal efficiency of 88.5% at an agitation speed of 50 rpm was reduced to 75% after increasing the agitation speed to 150 rpm. This reduction is the result of a degradation of flocs due to collisions between flocs at high agitation speeds.

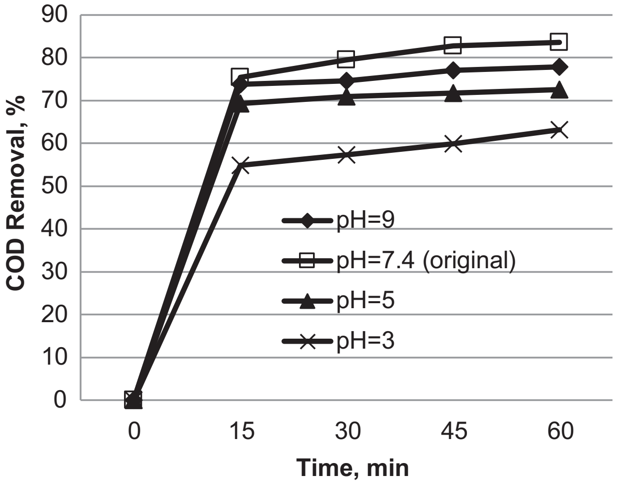

Fig. 7. The effect of pH on COD removal. *i*: 30 mA/cm^2, Na_2SO_4: 0.03 M, agitation speed: 100 rpm.

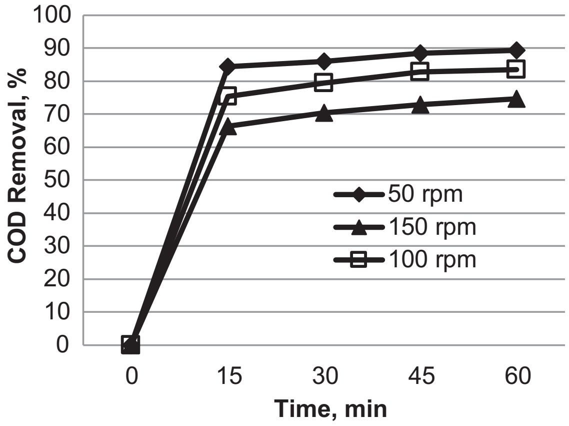

Fig. 8. The effect of agitation speed on COD removal. *i*: 30 mA/cm^2, Na_2SO_4: 0.03 M, pH 7.4.

4.5. Electro-Fenton process

Recently, Fenton oxidation has been investigated for the treatment of various types of wastewater. Ferrous or ferric ions react with H_2O_2 to generate a nonselective strong oxidant; hydroxyl radicals ($^{\cdot}OH$) [3,38]:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^- \tag{8}$$

Fenton’s reagent oxidizes the organic compound rapidly exothermically, primarily to carbon dioxide and water. In this part of the study, H_2O_2 was externally applied, while a sacrificial Fe anode was used as the Fe^{2+} source, and Fe^{2+} was continuously regenerated during electrolysis. Hydrogen peroxide was added at the start of the experiments to produce hydroxyl radicals rapidly and efficiently. H_2O_2 concentrations on removal efficiency were investigated, with the results being shown in Fig. 9. In the electro-Fenton process, a variation of iron (Fe^{2+}–Fe^{3+}) and an oxidation ability of hydroxyl radicals is strongly dependent on pH. As investigated in previous studies [3], the electro-Fenton process may be effective at lower pH values. Therefore, the effect of a H_2O_2 concentration was determined at pH 3. As can be seen from Fig. 9, at the start of the experiments, an 89% removal efficiency was achieved within the first 15 min, which may be due to the hydroxyl radicals produced. Over time, a limited improvement in removal efficiency was observed. Removal efficiencies of 89.3, 90.2, and 92.6% were obtained by adding 0.05, 0.1, and 0.2 M H_2O_2, respectively, while the maximum removal efficiency was 88.5% without any addition of H_2O_2. Therefore, it is clear that the highest COD removal was achieved using the electro-Fenton method.

An overall maximum COD removal of 92.6% was obtained at 30 mA/cm^2, 0.03 M Na_2SO_4, pH 3, an agitation speed of 50 rpm and an addition of 0.2 M H_2O_2. The initial COD concentration of 1,220 mg/L was reduced to 90 mg/L, which is below the national discharge standard of 125 mg/L. Thus, it is confirmed that the treatment of tissue paper wastewater to obtain a direct discharge standard can be achieved by coupling the Fenton reaction with EC.

4.6. The effect of electrode material

Electrode material is a significant parameter which affects removal efficiency. When the electrode material is changed, the sacrificing ion will also change. If aluminum or iron electrodes are used, respective $Al^{3+}_{(aq)}$ or $Fe^{3+}_{(aq)}$ ions are released from the anode and immediately undergo further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides.

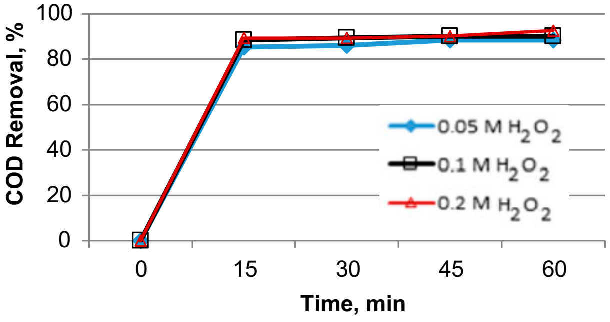

Fig. 9. The effect of H_2O_2 concentration on COD removal. *i*: 30 mA/cm^2, Na_2SO_4: 0.03 M, pH 3, agitation speed: 50 rpm.

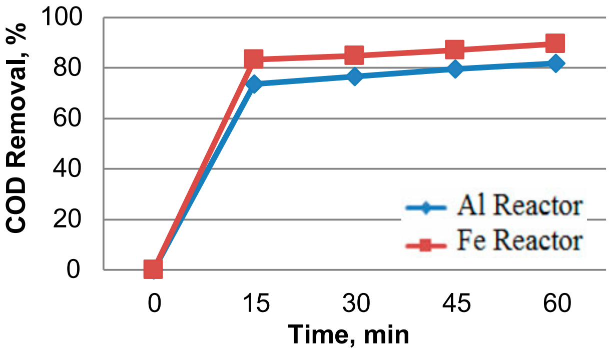

Fig. 10. The effect of electrode material on COD removal. *i*: 30 mA/cm^2, Na_2SO_4: 0.03 M, pH 7.4, agitation speed: 50 rpm.

In this study, the effect of electrode material was examined using iron and aluminum electrodes. The aluminum anode and cathode used were of the same shape and dimensions to that of the iron electrode described in Section 3.1.2.

As can be seen from Fig. 10, the iron electrode was found to be more effective than the aluminum electrode, with the iron electrode producing a removal efficiency of 88.5% and the aluminum producing 82%, respectively. This may be due to the greater amount of iron released from the anode compared with the amount of aluminum released. This is in agreement with Faraday's law, according to which the amount of iron ions released is approximately three times greater than aluminum ions under the same operating current, time, and electrode dimensions.

5. Result and discussion of the pyrolysis of electrocoagulation sludge

Lignocellulosic raw materials contain more than 400 different components that can be classified as aliphatics, phenol, methylphenols, methoxyphenols (guaiacols, syringols), carbonyl groups, fatty or organic acids, aromatics and PAHs, alcohols and furans. GC/MS is a preferred technique for identification and quantification of these components. As seen from the GC/MS data (Fig. 11), the phenol and its derivatives, nitrogen compounds, PAHs, and fatty acids were the major compounds detected in bio-oils. The bio-oil quality was improved using sludge as a catalyst. The degree of improvement was increased with an increasing additive amount of catalyst from 5 to 10%, at atmospheric pressure. The effect of the presence of sludge as a catalyst on the quality of the bio-oil obtained with catalytic pyrolysis is discussed in detail below.

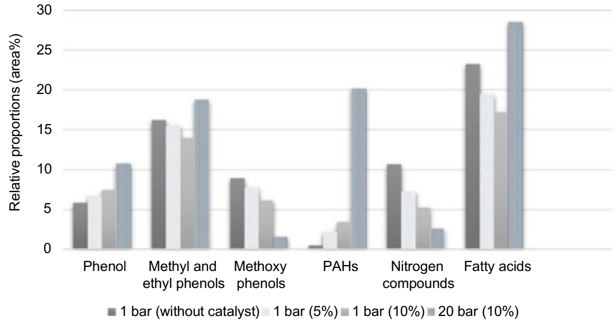

Fig. 11. Bio-oil component groups obtained from canola pyrolysis with/without sludge additive as a catalyst.

Phenol and its derivatives are related to the lignin component of the biomass. Phenols have a high commercial value. The concentration of phenol increased using sludge as a catalyst at atmospheric pressure, while that of methyl (phenol, 4-methyl, phenol, 3-methyl, phenol, 2,4-dimethyl, phenol, 2-methyl), ethyl (phenol, 3-ethyl), and methoxy phenols (phenol, 2-methoxy, phenol, 2-methoxy-4-methyl, 2-methoxy-4-vinylphenol, 2,6-dimethoxy phenol) decreased or vanished. In pressurized pyrolysis experiments, the trends of phenol and methoxy phenol concentrations were similar and those of methyl phenols were different from the trends obtained at atmospheric pressure. Using a catalyst, these compound formations decreased at atmospheric pressure, but they increased in pressurized atmosphere. The increase of phenol and the decrease of methoxy and methyl and ethyl phenols can be attributed to cracking reactions at atmospheric pressure. The oxygenated compounds in bio-oils, which make bio-oil more viscous, corrosive, less thermal, and chemically stable, make these oils unfit for utilizing as a transportation fuel. They are immiscible and must be treated before use. The catalyst leads to crack oxygenated and alkyl groups and then joins them to the gas phase. In addition, it effects the cracking and polymerization reactions in pressurized pyrolysis.

PAHs (naphthalene, 9H-Fluorene, phenanthrene, and anthracene) formation was significant at higher pressures. This may be due to polymerization reactions triggered by the catalyst, at long retention times.

In this study, the fatty acid components obtained, as a result of cracking reactions, were hexadecanoic acid, octadecanoic acid, and 9-octadecenoic acid. Their concentrations decreased at atmospheric pressure and increased in a pressurized atmosphere. This may be due to the pressurized atmosphere, which generally slows decarboxylation reactions, even when a catalyst is used. A similar observation was observed in our previous study [32].

Most of the nitrogenous components detected in the bio-oils were found to be of cyclic structure. Among them, benzenepropanenitrile, benzeneacetonitrile, benzonitrile, benzylnitrile, benzonitrile, 2,4,6,trimethyl, benzenamine, N-methyl, indole, 1H-indene, and 1-methyl are most important. The presence of these compounds in bio-oil is not desirable as they can lead to NO_x emissions. In our study, using the sludge as a catalyst, the concentration of these nitrogen compounds found decreased effectively at atmospheric pressure, as well as in pressurized pyrolysis experiments. This is a positive observation regarding the bio-oil quality.

6. Conclusion

In this study, electrocoagulation of tissue paper wastewater was performed using an iron disk turbine anode. Furthermore, solid waste sludge was used as a catalyst in the catalytic pyrolysis to obtain bio-oil in order to reduce any negative environmental effects of the sludge.

Based on the results achieved from the experiments, the following conclusions may be drawn:

(1) An overall maximum COD removal of 92.6% was obtained at 30 mA/cm^2, 0.03 M Na_2SO_4, pH 3, an agitation speed of 50 rpm, and the addition of 0.2 M H_2O_2. An initial COD concentration of 1,220 mg/L was reduced to 90 mg/L, which is below the national discharge standard of 125 mg/L. Therefore, it can be confirmed that the treatment of tissue paper wastewater to obtain the required discharge standard could be achieved by coupling the Fenton reaction with EC.

(2) The effect of a number of parameters, such as the supporting electrolyte concentration, current density, pH, agitation speed, H_2O_2 concentration, and the type of electrode material, was determined. It can be seen from the experiments that current density, Na_2SO_4 concentration, and H_2O_2 concentration have a positive effect on COD removal efficiency, while agitation speed has reciprocal impact. The best treatment efficiency was observed at the original pH of the wastewater (pH 7.4).

(3) The solid waste sludge of the electrocoagulation process was used as a catalyst in the catalytic pyrolysis to obtain bio-oil. It was found that the bio-oil quality improved using sludge as a catalyst, because the catalyst was effective in the cracking process of pyrolysis.

It can be concluded that the treatment of tissue paper wastewater was performed successfully. The waste sludge can be used as an iron source to produce bio-oil, using catalytic pyrolysis, with the waste being converted into a value-added product.

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