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Treatment of sugar industry wastewater by electrocoagulation using Fe and Al electrodes: a comparative study

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ABSTRACT

It was aimed in the present study to investigate the treatability of wastewater from sugar industry (WSI) using electrocoagulation method (EM) and the effects of system parameters (SPs) on removal yield (RY). SPs were chosen to be electrode material (ElM), initial pH (pH_i) of the solution, current density (CD), stirring speed (SS), type and concentration of support electrolyte. WSI collected from equalization pond of sugar production process in Erzurum Sugar Plant was used in the study. Aluminium and iron plate electrodes functioned as electrodes in the experiments, where additional supportive electrolyte in the solution increased the yield of COD removal and reduced the energy consumption. COD removal was found in the experiments conducted using aluminium electrode to be 97.43% at 180 min when CD, SS and pH_i were 2.143 mA cm^{-2}, 150 rpm and 6, respectively and by adding 100 mM NaCl while it was 67.24% at 180 min when iron electrode was used in the experiments and CD, SS and pH_i were 4.286 mA cm^{-2}, 150 rpm and 8, respectively by adding 100 mM NaCl.

Keywords: Sugar industry; Electrocoagulation; Al-Fe plate electrode; pH; Current density

1. Introduction

Sugar industry can be defined to be an industrial branch covering a production system where the products such as raw sugar, white sugar, powder sugar, brown sugar, dark kandis, yellow sugar, white kandis, liquid sugar, syrup for domestic and manufacturing use, sweetening syrup, artificial honey, molasses and spirit are produced from sugar beet or cane [1].

Since the content of WSI is mainly sugar, such wastewaters are polluted from one-way. In addition, sugar beet may contain nitrogen and phosphor and therefore, polluting parameters in WSI may be nitrogenous and phosphorus compounds. In addition to these compounds contained by sugar beets suspended solids from the soil and mud particles can be seen in WSI causing blurriness. Temperature should be taken into consideration as an important polluting parameter for WSI since several parts of the plant use cooling water. Based on the facts mentioned above, characteristics of the refinery WSI using sugar beet as raw material are BOD_5, COD, suspended solids, alkalinity, solved solids, nitrogen forms, total phosphor exchanges, total and fecal coliform, temperature and pH.

In electrocoagulation process, anode soluble Fe and Al ions are oxidized to Fe^{2+} and Al^{3+} forms while in cathode, as the result of the electrolysis of water, H^+ and OH^- ions are formed. OH^- ions are diffused in the solution and react to form $Fe(OH)_2$ or $Al(OH)_3$. During that time, organic and colloidal pollutants are subsidized simultaneously by with $Fe(OH)_2$ or $Al(OH)_3$ complex [2,3].

Electrode reactions when aluminium is used to be electrode material are as follows [4,5]:

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In anode:

$$Al \rightarrow Al^{3+} + 3e^{-} \quad (1)$$

In cathode:

$$2H_2O + 2e^{-} \rightarrow H_2\uparrow + 2OH^{-} \quad (2)$$

In the solution:

$$Al_{(aq)} + 3H_2O \rightarrow Al(OH)_{3(s)} + 3H^{+}_{(aq)} \quad (3)$$

In addition, depending on pH in aqueous medium, some types of aluminium compound can be seen as the result of the reaction $Al(OH)_2$, $Al_2(OH)^{2+}$ and $Al(OH)_4$. Al(H2O)63+, Al(H2O)5OH2+, Al(H2O)4OH2+ can be formed by hydrolysing Al^{3+} ions. In a wide pH range, several monomeric and polymeric hydrolysis products can be produced such as $Al(OH)^{2+}$, $Al_2(OH)_2^{4+}$, $Al(OH)^{4-}$, $Al_6(OH)_{15}^{3+}$, $Al(OH)^{4+}$, $A_{l8}(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$ and $Al_{13}(OH)_{34}^{5+}$ [2,3,6]. In the case of using iron as anode, two different mechanisms would be proposed in the formation of $Fe(OH)_n$(in the condition of n = 2 or 3). Anode and solution reactions are formed as follows [7,8]:

First Mechanism

Anode:

$$4Fe_{(s)} \rightarrow 4Fe_{(aq)}^{2+} + 8e^{-} \quad (4)$$

And with solved oxygen in solution;

$$4Fe^{2+} + 10H_2O + O_2 \rightarrow 4Fe(OH)_{3(s)} + 8H^{+} \quad (5)$$

Cathode:

$$8H^{+} + 8e^{-} \rightarrow 4H_{2(g)} \quad (6)$$

Eventually total reaction can be summarized as follows

$$4Fe + 10H_2O + O_2 \rightarrow 4Fe(OH)_3 + 4H_2 \quad (7)$$

Second mechanism:

Anode:

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^{-} \quad (8)$$

$$Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_2 \quad (9)$$

Cathode:

$$2H_2O_{(l)} + 2e^{-} \rightarrow H_{2(g)} + 2OH^{-}_{(aq)} \quad (10)$$

Ultimate total reaction can be summarised as follows;

$$Fe_{(s)} + 2H_2O_{(l)} \rightarrow Fe(OH)_{2(s)} + H_{2(g)} \quad (11)$$

Iron ions produced through electrochemical oxidation of iron electrode can produce monomeric $Fe(OH)_3$ ions and $Fe(H_2O)_6^{3+}$, $Fe(H_2O)_5(OH)^{2+}$, $Fe(H_2O)_4(OH^{)2+}$, $Fe_2(H_2O)$ $s(OH)_2^{4+}$ and $Fe_2(H_2O)_6(OH)_4^{4+}$ polymeric ions depending on pH of aquatic medium. Iron ions can be exposed to hydration depending on pH of the solution and form $Fe(OH)_2^{+}$, $Fe(OH)_2^{+}$, $Fe(OH)_3$ compounds under acidic conditions. In addition $Fe(OH)^{6-}$ and $Fe(OH)_4^{-}$ ions can be produced under alkali conditions [9].

2. Material and method

2.1. Material

WSI was taken from sugar refinery operated in the city of Erzurum processing about 3000 tonnes of sugar beet during a 73-d campaign period. Table 1 presents the characteristics of WSI used in experiments. Concentrated nitric acid and sodium hydroxide were used in the adjustment of b pH in WSI and all chemicals used in analyses were at analytic purity. Daily WSI flow rate from Erzurum Sugar Refinery is 6000 $m^3 d^{-1}$.

2.2.Experimental design

Electrocoagulation experiments were conducted using experimental design given in Fig. 1.

Table 1
Characteristics of WSI

Parameters	Range	Values
Specific conductivity (µs cm^{-1})	1350–1530	1460
BOD_5 (mg L^{-1})	725–950	800
Turbidity (NTU)	7.5–11	9.4
pH	5.0–5.35	5.17
COD (mg L^{-1})	2380–2700	2580

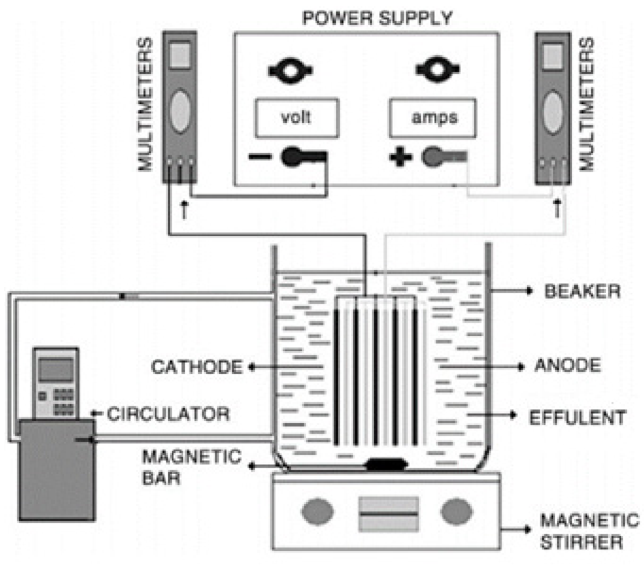

Fig. 1. Experimental set-up.

2.3. Experimental conditions and study intervals

In electrocoagulation studies, the operation ranges of parameters affecting the removal of COD of sugar wastewater are given in Table 2.

Reactor used in the experiments was made of Plexiglas material and its efficient volume is 3000 ml. Total amount of WSI used in experiments is 1100 ml.

Totally, 10 plate electrodes (5 anodes and 5 cathodes) were constructed with an effective surface area of 1400 cm^2 in the experiments. Distance between electrodes was adjusted to be 5 mm.

A digitally controlled direct current source (Shenzen-Mastech HY3005-3) was used for potential difference applied to the cell and current passing through the system and potential difference was measured using digital multimètre-rymen-201. Content of the reactor was stirred using a magnetic stirrer (Heidolph MR-3004) at predetermined rates. Temperature, pH and conductivity values of the solution were measured during the experiments using parameter measurer (WTW:H Cond 340i).

The removal yield of chemical oxygen demand (COD) and energy consumption [10,11] is calculated as follows:

$$\eta(\%) = \left(\frac{C_o - C_e}{C_o} \right) \quad (12)$$

$$W = \frac{I \cdot V \cdot t}{v} \quad (13)$$

where η is removal yield, C_e: final concentration of (COD) (mg L^{-1}), $C_{0:}$ initial concentration of (COD) (mg L^{-1}), *V*: cell voltage (V), *I*: current density (A), *t*: the operating time (minute) and ν: the volume of wastewater (L).

3. Results and discussion

3.1. Effect of stirring speed on the performance of the system

Fig. 2 represents graphically the effect of stirring speed on COD removal yield for 50, 150, 250 and 400 rpm. Experiments were conducted at natural pH of WSI, 5.20. During the experiment, current density was 1.429 mA cm^{-2} and temperature was 20°C.

Stirring speed parameter distributes equally flocculants in reactor formed as the result of the solution of electrode. Inefficient distribution causes inhomogeneous reactor content. In addition, stirring may cause the homogenisation of systemic variables such as temperature and pH [12].

When Fig. 2 is taken into consideration, the same trend is seem to be present in removal yield in the experiments conducted with both Al and Fe plate electrodes and the highest removal yield was 74% at a stirring speed of 150 rpm in Al plate experiments while 40.4% in those with iron plates. Removal yield values decreased in the experiments conducted below and above these speeds. At the stirring speed of 50 rpm, the reason for the decrease in removal yield may be inhomogeneous distribution of solved anode material, which accumulates in the bottom of reactor before reacting with pollutant. At other stirring speed, above 150 rpm, the reason for the decrease in removal yield is that in spite of the homogeneous distribution of electrochemically dissolved anode material, high stirring speed decreased flock formation trend and the formed flocks were fragmented depending on cutting force. Previous studies confirmed similar effects of stirring speed on COD removal yield [13,14].

3.2. Effect of initial pH on the performance of the system

Among the most important parameters in electrocoagulation is pH_i of WSI [15,16]. Since pH of unprocessed WSI can affect the stability of hydroxide types, it may also have effect on pollutant removal yield. As the result of anode and cathode reactions, pH of WSI can change. Therefore, based on pH of WSI, electrolytic soluble metal ions (Al^{3+}, Fe^{2+} etc.) can form different metal hydroxide types at different pH values.

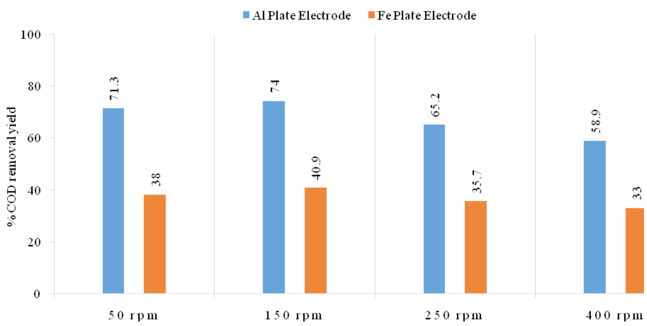

Fig. 2. The effect of stirring speed on COD removal yield (pH_i: 5.20; CD: 1.429 mA cm^{-2}; T:20°C).

Table 2
Study intervals of parameters affecting COD removal of WSI

Parameters	Chosen parameter ranges	
	Al Plate Electrode	Fe Plate Electrode
Stirring Speed (rpm)	50-150-250-400	50-150-250-400
İnitial pH	3-4-5-6-7	4-5-6-7-8-9
Current Density (mA cm^{-2})	0.714-1.429-2.143-2.857-3.571	0.714-1.429-2.143-2.857-3.571-4.286
Supporting electrolyte type	50 mM NaCl – 50 mMKCl – 50 mM Na_2SO_4 – 50 mM $NaNO_3$	50 mM NaCl - 50 mMKCl – 50 mM -Na_2SO_4 – 50 mM $NaNO_3$
Supporting electrolyte concentration (NaCl mM)	25-50-75-100	25-50-75-100

Effect of pH_i was investigated with Al plate electrode in the range of pH 3–7 and Fe plate electrode in the range of pH 4–9. Results obtained are given graphically in Fig. 3. It is seen when Fig. 3 is considered that the highest COD removal yield is 83% with Al plate electrode at pH 6 and 50.31% with Fe plate electrode at pH 8. It can also be seen when Fig. 3 is taken into consideration that COD removal yield through electrocoagulation process from WSI is strongly associated with pH_i of wastewater. Changes in pH were followed during the experiments and the results are given in Table 3, where it is seen that there is a gradual increase in pH of WSI as the result of the reactions at cathode. Previous studies also showed such formations in the system (Bayar et al., 2014). Such a result might have come caused from the formation of Al and Fe types with high coagulation effect at pH 5.5–8.5 and 6–9 ranges for Al and Fe plates respectively by considering the activity diagrams of Al and Fe based on pH in medium [4,17–19]. COD removal yield is expected to decrease since out of these pH ranges solubility of Al and Fe types will decrease.

3.3. Effect of current density on system performance

Current density helps determine the amount of aluminium and iron leaving electrodes in electrocoagulation process, formation rate and size of gaseous bulbs and the development of flocks [3,20]. It is therefore one of the most important parameters affecting pollutants' removal yield. The effect of current density on COD removal yield was investigated in the range of 0.714–3.571 mA cm^{-2}. Stirring speed was fixed at 150 rpm in experiments and pH_i was 6 and 8 for Al and Fe plate electrodes, respectively. Fig. 4 shows graphically COD removal yield.

Depending on the increase in current density applied to the system the dissolution rate of Al and Fe also increases and larger amount of flocculants are formed. At fixed pollutant amount, larger $Al(OH)_3$, $Fe(OH)_2$ and $Fe(OH)_3$ rates react and remove more pollutant from the medium. Depending on the increase in current density, density of bulbs and formation rates also increase and their sizes get smaller. Such a situation can result in H_2 flotation and cause pollutants to be removed faster at higher rates [3,21,22].

Energy consumption was calculated using the Eq. (13) and the data obtained from the experiments where the effects of current density on the pollutant removal yield from WSI. Results are presented graphically in Fig. 5. As the current density increased potential difference applied on the system and thus increasing energy consumption [14,16,23].

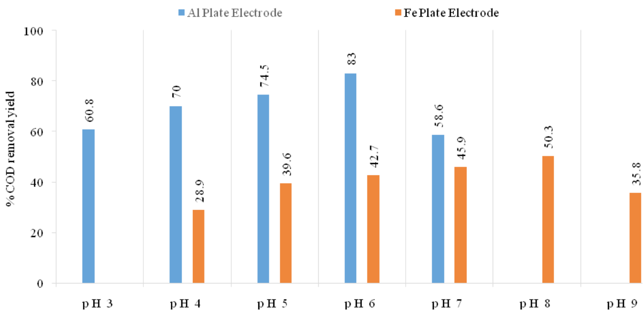

Fig. 3. The effect of initial pH on COD removal yield (SS: 150 rpm; CD: 1.429 mA cm^{-2}; T: 20°C).

Table 3
The change of pH during reaction time

	Time (minute)	pH 3	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9
Al plate electrode	0	3.0	4.0	5.0	6.0	7.0	–	–
	180	5.10	5.65	6.22	6.98	7.65	–	–
Fe plate electrode	0	–	4.0	5.0	6.0	7.0	8.0	9.0
	180	–	7.38	8.89	9.21	9.4	9.63	10.23

3.4. Effect of the type and concentration of support electrolyte on the performance of the system

Effect of support electrolyte concentration on COD removal yield was determined through the experiments where Al and Fe plate electrodes were used under optimum experimental conditions with 50 mmol NaCl, $NaNO_3$, Na_2SO_4 and KCl. The highest COD removal yield in the experiments was determined in the presence of 50 mmol NaCl (96% for Al plate; 64% for Fe plate). Data obtained are presented graphically in Fig. 6.

Following these experiments, additional experiments were conducted by adding 25, 50, 75 and 100 mmol NaCl to WSI under the same conditions. Data obtained is shown graphically in Fig. 7.

When considered Fig. 7, it is seen that the effect of support electrolyte concentration (SEC) on COD removal yield in WSI is lower. In such systems, support electro-

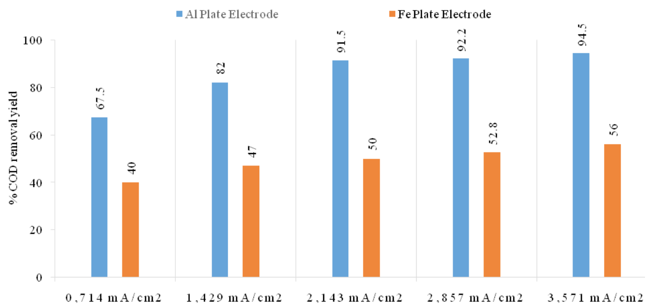

Fig. 4. The effect of current density on COD removal yield (SS: 150 rpm; pH_i(Al): 6; pH_i(Fe): 8; T: 20°C).

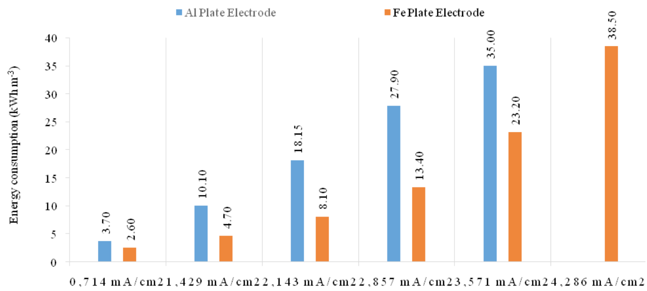

Fig. 5. The effect of current density on energy consumption (SS: 150 rpm; pH_i(Al): 6; pH_i(Fe): 8; T: 20°C).

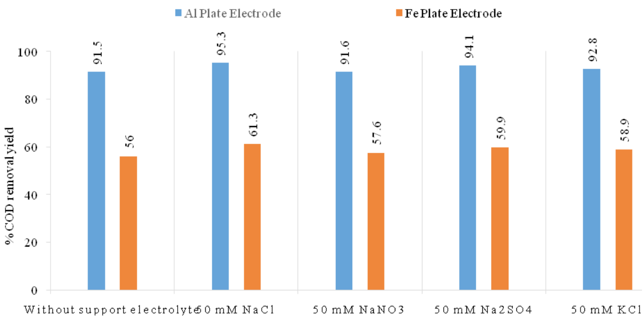

Fig. 6. The effect of support electrolyte type on COD removal yield (SS: 150 rpm; pH_i(Al): 6; pH_i(Fe): 8; CD(Al): 2.143 mA cm^{-2}; CD(Fe): 4.286 mA cm^{-2}; T: 20°C).

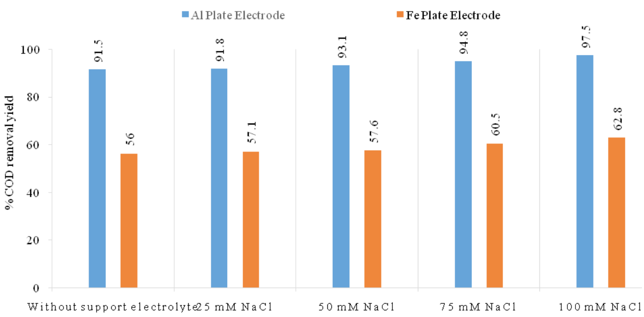

Fig. 7. The effect of NaCl concentration on COD removal yield (SS: 150 rpm; pH_i(Al): 6; pH_i(Fe): 8; CD(Al): 2.143 mA cm^{-2}; CD(Fe): 4.286 mA cm^{-2}; T: 20°C).

lyte is used in the system to form more flocculants and increases the conductivity of solution. Therefore, for wastewater with lower specific conductivity, the use of support electrolyte generally increases removal yield. The highest treatment yield was obtained to be 98% with Al plate electrode when added 100 mmol NaCl while it was 67.9% with Fe plate.

Data obtained from the experiments where the effect of supporting electrolyte concentration on COD removal yield was investigated was used to calculate energy consumption values through Eq. (13). Trend of energy consumption in the system over time for various supporting electrolyte concentrations is shown graphically in Fig. 8. When considered Fig. 8, increase in supporting electrolyte concentration is thought to decrease energy consumption. The reason for this is that supporting electrolyte rate added in the system increased the connectivity of WSI. Such a situation may cause a decrease in potential required for the passage of the same current density through the system. Therefore, energy consumption of the system also decreases.

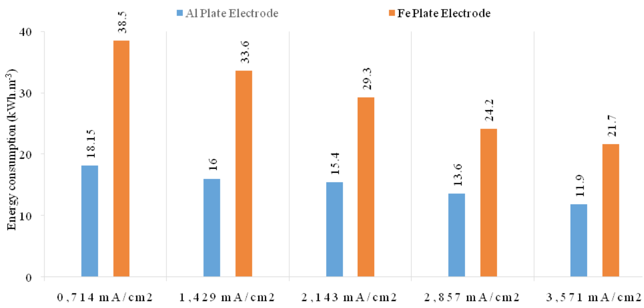

Fig. 8. The effects of NaCl concentrate on energy consumption (SS: 150 rpm; pH_i(Al): 6; pH_i(Fe): 8; CD(Al): 2.143 mA cm^{-2}; CD(Fe): 4.286 mA cm^{-2}; T: 20°C).

4. Conclusion

It was aimed in the present study to investigate the treatability of WSI collected from equalization pond in Erzurum Sugar Refinery employing electrocoagulation method and determine the effects of SPs on removal yield. SPs were chosen to be electrode material (ElM), initial pH (pH_i) of the solution, current density (CD), stirring speed (SS), type and concentration of support electrolyte. Easily available, affordable and efficient aluminium and iron electrodes were chosen to be electrode materials. The largest COD removal yield was obtained through Al electrodes. In the experiments where the effect of SR on removal yield was investigated, the largest yield was achieved in both Al and Fe plate electrodes at a SR of 150 rpm. Effect of pH on COD removal yield was investigated in pH range 3–7 for Al plate while 4–9 for Fe plate. The highest yield rate was found to be 83% at pH 6, and minimum concentration of $Al(OH)_3$ on Al plate electrode while at pH 8 when the concentration of $Fe(OH)_3$ and $Fe(OH)_2$ was minimum on Fe plate, yield rate was 50.31%. Increase in CD in the experiments conducted using both plates resulted in the increases of both COD removal yield and energy consumption. It was determined from the experiments that both the type and concentration of support electrolyte had no significant effect on the removal yield of the system. The largest removal yield was achieved in the experiments conducted with 100 mM NaCl to be 97.43% for Al plate and 67.24% Fe plate.

References

[1] E. Zeytinoğlu, Türkiye'deki Şeker Endüstrisi. Şeker Endüstrisi Yayınları, İskender Matbaası, İstanbul, 1964.
[2] A. Gürses, M. Yalçin, C. Doğar, Electrocoagulation of some reactive dyes: a statistical investigation of some electrochemical variables, Waste Manag., 22 (2002) 491–499.
[3] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol., 38 (2004) 11–41.
[4] S. Bayar, R. Boncukcuoğlu, A.E. Yilmaz, B.A. Fil, Pre-treatment of pistachio processing industry wastewaters (PPIW) by electrocoagulation using Al plate electrode, Sep. Purif. Technol., 49 (2014) 1008–1018.
[5] B. Khemila, B. Merzouk, A. Chouder, R. Zidelkhir, J.-P. Leclerc, F. Lapicque, Removal of a textile dye using photovoltaic electrocoagulation, Sustain. Chem. Pharm., 7 (2018) 27–35.
[6] F.I.A. Ponselvan, M. Kumar, J.R. Malviya, V.C. Srivastava, I.D. Mall, Electrocoagulation studies on treatment of biodigester effluent using aluminum electrodes, Water, Air, Soil Pollut., 199 (2009) 371–379.
[7] Y. Yavuz, Ü.B. Ögütveren, Treatment of industrial estate wastewater by the application of electrocoagulation process using iron electrodes, J. Environ. Eng., 207 (2018) 151–158.
[8] Y.Ş. Yildiz, A.S. Koparal, Ş. İrdemez, B. Keskinler, Electrocoagulation of synthetically prepared waters containing high concentration of NOM using iron cast electrodes, J. Hazard. Mater., 139 (2007) 373–380.

[9] M.Y.A. Mollah, R. Schennach, J.R. Parga, D.L. Cocke, Electrocoagulation (EC) — science and applications, J. Hazard. Mater., 84 (2001) 29–41.

[10] A.S. Koparal, Y.Ş. Yildiz, B. Keskinler, N. Demircioğlu, Effect of initial pH on the removal of humic substances from wastewater by electrocoagulation, Sep. Purif. Technol., 59 (2008) 175–182.

[11] M. Kobya, U. Gebologlu, F. Ulu, S. Oncel, E. Demirbas, Removal of arsenic from drinking water by the electrocoagulation using Fe and Al electrodes, Electrochim. Acta, 56 (2011) 5060–5070.

[12] S. Bayar, Y.Ş. Yıldız, A.E. Yılmaz, Ş. İrdemez, The effect of stirring speed and current density on removal efficiency of poultry slaughterhouse wastewater by electrocoagulation method, Desalination, 280 (2011) 103–107.

[13] S. Özcan, M.T. Yılmaz, S. Bayar, Erzurum Şeker Fabrikası Atıksularının Elektrokoagülasyon Prosesi ile Arıtılmasında Akım yoğunluğu ve Karıştırma Hızının Etkisi, Iğdır University J. Inst. Sci. Technol., 4 (2014) 9.

[14] A.E. Yilmaz, R. Boncukcuoğlu, M.M. Kocakerim, M.T. Yilmaz, C. Paluluoğlu, Boron removal from geothermal waters by electrocoagulation, J. Hazard. Mater., 153 (2008) 146–151.

[15] N. Adhoum, L. Monser, Decolourization and removal of phenolic compounds from olive mill wastewater by electrocoagulation, Chem. Eng. Process., 43 (2004) 1281–1287.

[16] P. Ratna Kumar, S. Chaudhari, K.C. Khilar, S.P. Mahajan, Removal of arsenic from water by electrocoagulation, Chemosphere, 55 (2004) 1245–1252.

[17] Ş. İrdemez, N. Demircioğlu, Y.Ş. Yildiz, The effects of pH on phosphate removal from wastewater by electrocoagulation with iron plate electrodes, J. Hazard. Mater., 137 (2006) 1231–1235.

[18] M. Kobya, E. Demirbas, Evaluations of operating parameters on treatment of can manufacturing wastewater by electrocoagulation, J. Water Process Engineer, 8 (2015) 64–74.

[19] M. Zaied, N. Bellakhal, Electrocoagulation treatment of black liquor from paper industry, J. Hazard. Mater., 163 (2009) 995–1000.

[20] M. Uğurlu, A. Gürses, Ç. Doğar, M. Yalçın, The removal of lignin and phenol from paper mill effluents by electrocoagulation, J. Environ. Eng., 87 (2008) 420–428.

[21] O. Abdelwahab, N.K. Amin, E.S.Z. El-Ashtoukhy, Electrochemical removal of phenol from oil refinery wastewater, J. Hazard. Mater, 163 (2009) 711–716.

[22] B. Merzouk, B. Gourich, A. Sekki, K. Madani, M. Chibane, Removal turbidity and separation of heavy metals using electrocoagulation–electroflotation technique: A case study, J. Hazard. Mater., 164 (2009) 215–222.

[23] P. Gao, X. Chen, F. Shen, G. Chen, Removal of chromium(VI) from wastewater by combined electrocoagulation–electroflotation without a filter, Sep. Purif. Technol., 43 (2005) 117–123.