

Treatment of Train Industry Oily Wastewater by Electrocoagulation with Hybrid Electrode Pairs and Different Electrode Connection Modes

Fuat Ozyonar

Department of Environmental Engineering, Cumhuriyet University, 58140 Sivas, Turkey

E-mail: fozyonar@cumhuriyet.edu.tr

Received: 13 November 2015 / Accepted: 29 November 2015 / Published: 1 January 2016

In this study, treatability of oily wastewater from train industry part washing machine was investigated by electrocoagulation process with aluminum, iron and hybrid electrodes (eight different combinations) and different electrode connection modes (series and parallel) in a batch reactor. The removal efficiencies for chemical oxygen demand (COD), total organic carbon (TOC) and turbidity were evaluated and the effects of different operating parameters such as electrode type (eight combinations), initial pH (4-10), current density (25-150 A/m²), air injection flow (0-6 L/min), electrode surface area (210-630 cm²) and connection mode (monopolar parallel, monopolar series and bipolar series) were investigated. The optimum operating conditions were identified as Fe-Al-Fe-Al (anode-cathode-anode-cathode) hybrid electrodes, initial pH of 6, current density of 75 A/m², air injection flow of 2 L/min, electrode surface area of 210 cm² and monopolar series (MP-S) mode. Under optimum operation conditions, removal efficiencies for COD, TOC and turbidity at 5 min operating time were respectively obtained to be 94.5%, 79.5% and 98.5%. The optimum operation cost at MP-S connection mode and hybrid electrode type was calculated as 0.60 \$/m³. Current results revealed that the best results in EC process for pollutant removal from oily wastewater of train part washing machine could be achieved with Fe-Al-Fe-Al electrode pairs in MP-S electrode connection mode.

Keywords: Electrocoagulation, Hybrid Fe-Al electrode, Electrode connection mode, Oily wastewater, COD removal.

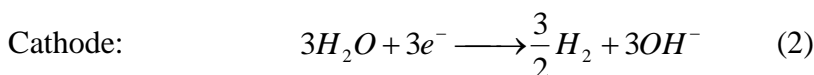
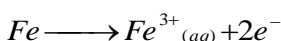
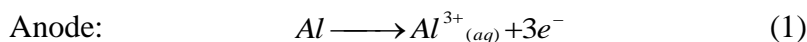
1. INTRODUCTION

Oily wastewater occurs widely in metal and mechanical industries. Train construction and repair industry also create significant amount of oily wastewater. Repair and process water may

generate significant amounts of oil, grease and surfactants. Oil can present in waters in three different fashions [1, 2]; as immiscible matter, unstable emulsion and oily emulsion. The first type can easily be separated from water by using suitable physicochemical treatment processes. In the second and the third types, oily wastewater is highly stable so removal of unstable emulsion and oily emulsions is quite difficult through conventional treatment processes [3]. Various classic treatment processes and advanced techniques have been used for the treatment of oily wastewater. These techniques include membrane processes (microfiltration, ultrafiltration and membrane bioreactor) [4-5], chemical coagulation and flocculation [6-8], flotation or dissolved air flotation [9, 10], biological treatment [11, 12], electrochemical processes; electro-flotation (EF) [13, 14], electrocoagulation (EC) [15, 16], electrooxidation (EO) [17, 18].

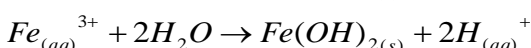
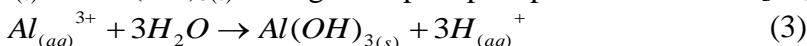
Electrochemical treatment processes (EF, EC and EO) are advanced treatment process. EC process is a common primary treatment technique among the electrochemical treatment processes. EC process has some advantages such as high removal efficiency, no chemical addition, decreased amount of sludge, versatility, energy efficiency, safety, selectivity, amenability and lower operational cost. The EC process has three main steps; (1) electrolytic reaction at the surface of electrode, (2) formation of coagulants in the aqueous phase, (3) adsorption of soluble or colloidal particles onto coagulants and removal by sedimentation or flotation [19-21]. Generally, iron or aluminum electrodes are used in EC process since these electrodes are cheap and easily accessible [22, 23, 24].

Main chemical reactions that occurred at anode and cathode are provided below;



While these reactions occurring, H^{+} ions or OH^{-} ions are likely adhered to the electrodes in acidic or alkaline media, respectively [25, 26, 27].

Fe, Al and OH^{-} ions generated by electrode reactions mentioned above and These metals will react to form various hydroxides and/or polyhydroxides species in reaction medium (such as $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^{+}$, $\text{Al}_2(\text{OH})_2^{4+}$, Fe (OH)₂ hydroxide species; $\text{Al}_6(\text{OH})_{15}^{3+}$, $\text{Al}_7(\text{OH})_{17}^{4+}$, $\text{Al}_8(\text{OH})_{20}^{4+}$, $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$, $\text{Al}_{13}(\text{OH})_{34}^{5+}$, $\text{Fe}(\text{H}_2\text{O})_6^{2+}$, $\text{Fe}(\text{H}_2\text{O})^{2+}$, $\text{Fe}(\text{H}_2\text{O})_4(\text{OH})^{2+}$, $\text{Fe}_2(\text{H}_2\text{O})_8(\text{OH})_2^{4+}$ and $\text{Fe}_2(\text{H}_2\text{O})_6(\text{OH})_4^{4+}$ polyhydroxides species) depending on pH range of the media. Above pH>9, $\text{Al}(\text{OH})^{4-}$ and $\text{Fe}(\text{OH})^{4-}$ are the dominant species. These species will be transformed finally into $\text{Fe}(\text{OH})_{2(s)}$ and $\text{Al}(\text{OH})_{3(s)}$ through complex precipitation reactions [28, 29].



The soluble or colloidal species onto coagulants are adsorbed before the sedimentation or flotation will be achieved removal of the pollutants. $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ have huge surface area which is highly helpful aimed at fast adsorption of soluble organic compounds onto floc surface [25, 26, 27]. These occurring flocs can be polymerized to form $\text{M}_n(\text{OH})_{3n}$ after adsorption stage and can easily be removed from aqueous medium by sedimentation and flotation [27, 28, 29].

The treatment of oily wastewater from various industries by EC process was reported in the literature [1, 2, 30-33]. But, most of the researches on treatment of oily wastewater by the EC used Al or Fe electrode and only connection mode. Still, further studies are required to elucidate the effect of different electrode configurations and connection modes. Chen [29] and Mollah et al [19] described various typical configurations for EC electrode and connection modes. Besides, they reported the advantage and disadvantages of such configurations and modes. The previous studies have not investigated two important parameters such as hybrid electrode configurations and different connection modes.

The present study was conducted to investigate the effects of Al, Fe and Al-Fe hybrid electrodes (eight different configurations), type of the electrolytic cell connection modes (monopolar parallel, monopolar series, bipolar series configurations), initial pH, current density, air injection flow, electrode surface area and operation time on the removal COD, TOC and turbidity from oily wastewater of train industry. The optimum hybrid electrode configuration, the electrolytic cell connection and other parameters were determined. Operating cost was calculated for EC process.

2. MATERIAL AND METHOD

The oily wastewater used for the EC process was supplied from train industry in Sivas. The wastewater from the bottom effluent of part washing machine was taken (Figure.1). The part washing machine cleans oil and grease over various train steel parts. The washing machine water is prepared from mixture of water and solvent. So, the wastewater contains oil–grease and surfactants. The characteristics of train part washing machine wastewater (TPWMWW) can be seen in Table 1.

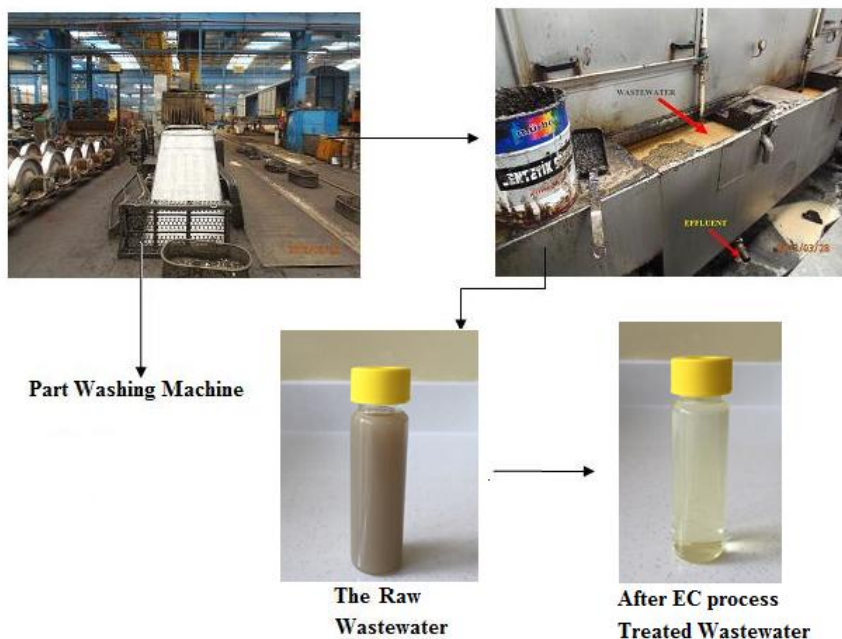


Figure 1. The part washing machine, effluent wastewater and treated wastewater by EC process.

Table 1. Characteristics of experimental TPWMWW

Parameter	Value
COD (mg/L)	4400
TOC (mg/l)	2560
BOD ₅ (mg/L)	710
Oil-Grease (mg/L)	1000
Electrical Conductivity (μs/cm)	850
pH	9.1
TSS(mg/L)	58

The experiments were carried out in a batch mode using a 1000 mL Plexiglas reactor (130x100x100 dimension) by vertically Fe-Al electrodes spaced 20 mm apart and dipped into the reactor (Figure 2). At the experiments, the electrodes were used to determine the optimum hybrid electrode pairs (Anode-Cathode-Anode-Cathode), which have made of aluminum and iron plate with dimensions of 50x70x2 mm (99.5% purity). The EC experiments were conducted by using only aluminum, only iron and also hybrid electrodes that were designed with aluminum and iron electrodes together as two anode and two cathode using different eight combinations of Fe-Al-Fe-Al, Fe-Al-Al-Fe, Al-Fe-Fe-Al, Al-Fe-Al-Fe, Fe-Al-Al-Al, Al-Fe-Fe-Fe hybrid electrodes and Al-Al-Al-Al or Fe-Fe-Fe-Fe all of electrodes. The electrodes were connected to monopolar series, monopolar parallel and bipolar series and a digital DC power supply (Alpha 10A-50V) and equipped with galvanostatic operational options [37-39]. The total electrode surface area was adjusted as 210, 420 and 630 cm².

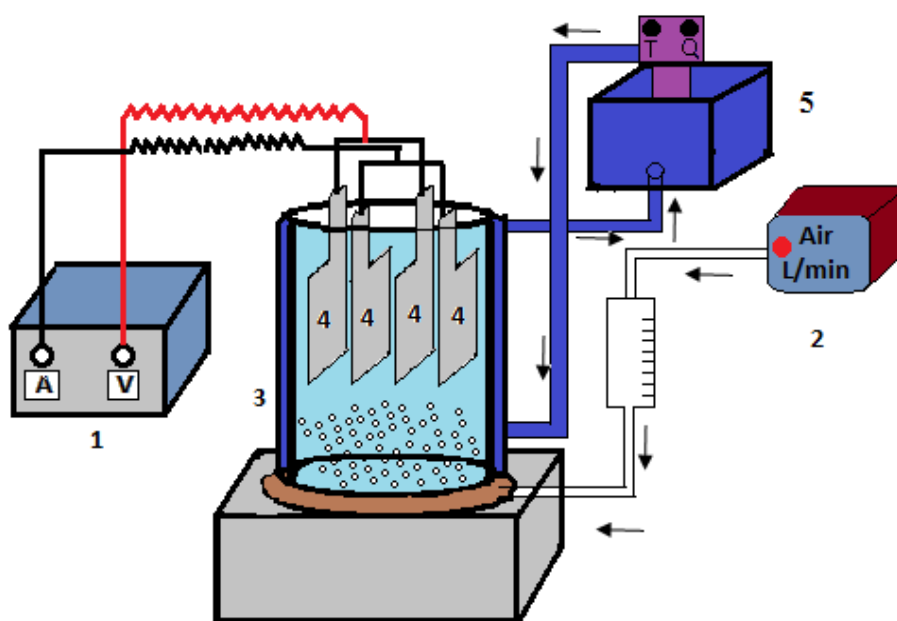


Figure 2. The schematic diagram of electrocoagulation process (1. Power supply, 2. Air flowmeter, 3. EC reactor, 4. Al, Fe or Al-Fe hybrid electrodes, 5. Water circulator).

The experiments were carried out at constant temperature (25°C) through a water circulator and with 1000 mL of wastewater solution. Before each experiments, electrodes with acetone to remove surface grease-oily and pollutants were washed, then matters on electrode surfaces were cleaned by dipping for 1 min into a solution freshly prepared by mixing 100 mL of HCl solution (35%) and 200 mL of hexamethylenetetramine aqueous solution (2.80%) [26]. Then electrodes were washed with pure water for the removal of the residuals on their surfaces and dried by oven. The next step of the experiment was started.

Chemical oxygen demand (COD) analysis was carried out as indicated in the standard analysis methods [34]. Biological oxygen demand (BOI₅) was determined by respirometric method (Oxitop IS6, German); Total organic carbon (TOC) were measured by burning of the samples at 680 °C using a non-dispersive IR source (Tekmar Dohrmann, Apollo 9000, USA); the UV-Vis spectra of samples were measured by using a UV-Vis spectrophotometer (Merck spectroquant Pharo 300, German). The turbidity was measured using a turbidity meter (Micro TPI, HF scientific, USA). The pH and electrical conductivity of the samples were measured by means of a pH meter (C931, Consort, Belgium) and a conductivity meter (340i, WTW, German).

The percentage removal efficiency of COD, TOC and turbidity was calculated using the following equation, Eq. (4).

$$\text{Percentage removal efficiency (\%)} = \left(\frac{C_0 - C}{C_0} \right) \times 100 \quad (4)$$

The one of the most important parameters in EC processes is operating cost for the reason that the operating cost effects the application of any method of wastewater treatment. The operating cost includes material (mainly electrodes) cost, electrical energy cost, labor, maintenance and other costs [40]. In this study, the operating cost was calculated together with electrodes, electrical energy, chemical costs and air pump electrical energy cost. So, energy, electrode and chemical consumption costs were taken into account as major cost items [26]. Calculation of operating cost is expressed as;

$$\text{Operating Cost} = A \text{Energy consumption} + B \text{Electrode consumption} + C \text{Chemical consumption}$$

Where energy consumption and electrode consumption are consumption quantities per m³ of wastewater treated. *A*, *B* and *C* given for the Turkish Market at August 2015, Which are as electrical energy price 0.079 \$/kWh, electrode material price 0.91 \$/kg for iron, 1.21\$/kg for aluminum electrode and chemical costs 0.8 \$/kg for NaOH, and 0.33 \$/kg for H₂SO₄.

During the EC process, the electrode and energy consumptions were calculated by using the following equations;

$$\text{Energy}_{\text{consumption}} = \frac{(V.I.t)}{v} \quad (5)$$

.....Where Energy_{consumption} is energy consumption (kWh/m³), V is voltage (Volt), I is current (Ampere), t is EC time (s) and v is volume of the treated wastewater (m³), respectively. Electrode material consumption was determined by weighing the start and end of the electrode weight. The charge loading are calculated in the following equations, according to Faradays law;

$$\frac{\text{Faraday}}{m^3} = \frac{(I.t)}{(F.v)} \quad (6)$$

$$\text{Electrode}_{\text{consumption}} = M_s - M_f \quad (7)$$

.....Where F is Faraday’s constant (96485 C/mol). M_s is starting electrode weight, M_f is ending electrode weight.

3. RESULT AND DISCUSSION

Treatability of TPWMWW by electrocoagulation process was investigated by using Al and Fe electrodes. So as to evaluate optimum operation conditions, the experiments were carried out with different electrode types (eight configurations), initial pH (4-10) levels, current densities (25-150 A/m²), air injection flows (0-6 L/min), electrode surface areas (210-630 cm²), electrode connection modes (MP-P, MP-S, BP-S) and operation times (0-45min).

3.1 Effect of electrode type

The electrode type is a very important factor influencing the removal performance of EC process [35, 36, 37]. The effects of different electrodes types on treatment of TPWMWW are shown in Figure 3. Fe and Al plate electrodes in eight different hybrid configurations were used to find out the optimum electrode pairs (anode-cathode) for the highest removal efficiencies for COD, TOC and turbidity. In order to investigate the effects of electrode type, experiments were carried out at initial pH of 6, current density of 75 A/m², air injection flow of 2 L/min, electrode surface area of 210 cm² and electrode connection mode of MP-P.

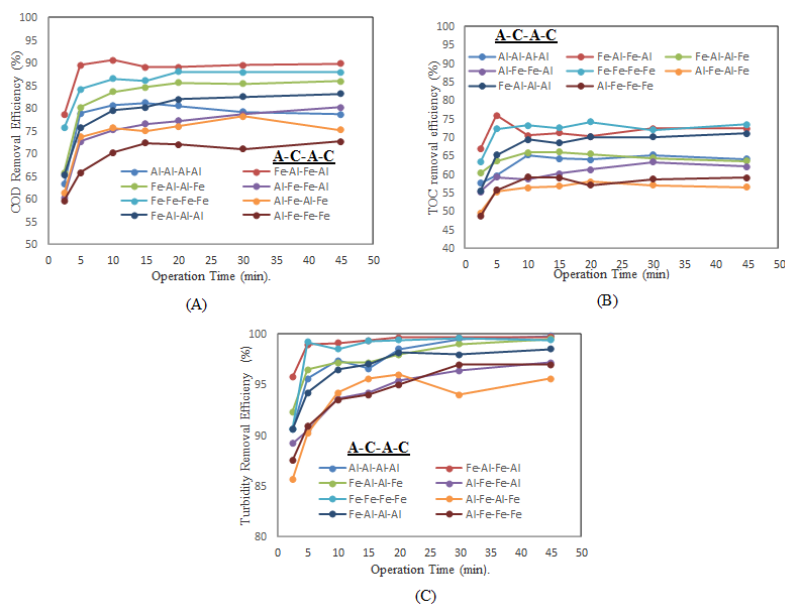


Figure 3. Effect of hybrid electrode types on removal efficiency of COD (A), TOC (B) and turbidity (C) (A: Anode, C: Cathode) (Operating conditions: pH = 6, current density = 75 A/m², air injection flow = 2 L/min, electrode surface area = 210 cm² and electrode connections mode = MP-P).

As seen in Figure 3, the principle removal of pollutants was observed within 5-10 min. The highest removal efficiency for COD was obtained as 90.6% in 10 min with Fe-Al-Fe-Al hybrid electrode pairs. The removal efficiency for COD with the other hybrid electrode pairs of Fe-Fe-Fe-Fe, Fe-Al-Al-Fe, Al-Al-Al-Al, Fe-Al-Al-Al, Al-Fe-Al-Fe, Al-Fe-Fe-Al and Al-Fe-Fe-Fe in 10 min were respectively found to be 86.5%, 83.6%, 80.6%, 79.5%, 75.6%, 75.2%, 70.2%. The highest and fastest removal of COD was obtained with Fe-Al-Fe-Al electrode pairs. Fe-Al-Fe-Al electrode pairs were found to be more suitable than other pairs because it had a shortest time (10 min) of removal. Considering the other performance parameters, the highest removal efficiencies for TOC and turbidity were respectively obtained as 75.6% and 99% with Fe-Al-Fe-Al electrode pairs in 5 min. Fe-Al-Fe-Al electrode pairs were seemed to be the best choice with respect to removal efficiencies and EC operation time. The removal efficiency for COD with Fe-Al-Fe-Al electrode pairs in 5 min operating time was 89.5%. Besides, operating costs at 5 min and 10 min were calculated as 0.24\$/m³ and 0.49\$/m³, respectively. According to the results with respect to operating costs and performance parameters, the operating time of 5 min was found to be suitable. In a similarly study, Kobya et al [37] reported the highest removal of arsenic with Fe-Al-Al-Fe electrode pairs. According to Kobya et al [37], because of shorter time for higher removal of pollutants, the electrochemical equivalent masses for Al and Fe were 5.59 and 17.37 mg/A min. So, theoretically iron anodes with the same electrical charge produces more coagulants than Al anodes. This event may be the reason for the higher removal of pollutants at short operating time when using hybrid electrode configurations [37]. Generally, the removal mechanism of pollutants in the EC process was adsorption, coprecipitation and flotation. The pollutants on freshly formed Al(OH)₃ and Fe(OH)₃ flocs were adsorbed and coprecipitated. These metal hydroxyl flocs via hydrogen bubbles formed at the cathode undergo floatation [38,39].

3.2 Effect of initial pH

The initial pH is very important parameter removal of pollutant in the EC process [23, 24]. Generally, the optimum initial pH range for wastewater treatment should be range 5 – 8 [41, 42]. The pH of 4, 6, 8 and 10 were tested in this study. All these experiments were carried out at constant conditions; Fe-Al-Fe-Al electrodes configurations, current density of 75 A/m², air injection flow of 2 L/min, electrode surface area of 210 cm³ and connection mode of MP-P.

As seen in Figure 4, the highest removal efficiencies for COD and TOC was observed at a pH of 6 and the removal efficiencies decreased at other pH values. But, the removal efficiencies for turbidity in all pH values were not significantly different from each other. According to Kobya et al [38], Modirshahla et al [42] and Found [30], decreased removal efficiencies of pollutants were observe at strong alkaline conditions with pH>9. This may be explained with the occurrence of monomeric anions of Fe(OH)₄ and Al(OH)₄ at alkaline pH levels. These forms of metal hydroxides are not suitable for treatment of wastewaters [38-39-41-42]. The other researchers in their studies found to be around neutral pH of optimum initial pH [23, 24, 41, 42]. Fouad [30] found that initial pH in the oily wastewater treatment by EC process was 7. In addition, the pourbaix diagrams of the iron and aluminum flocks in aqueous solutions showed that the highest removal of pollutant from wastewater

were obtained with neutral or slight neutral $4 < \text{pH} < 10$. This pH level seen with this study. Thus, optimum initial pH was selected as $\text{pH} = 6$ for better removal efficiencies for COD, TOC and turbidity.

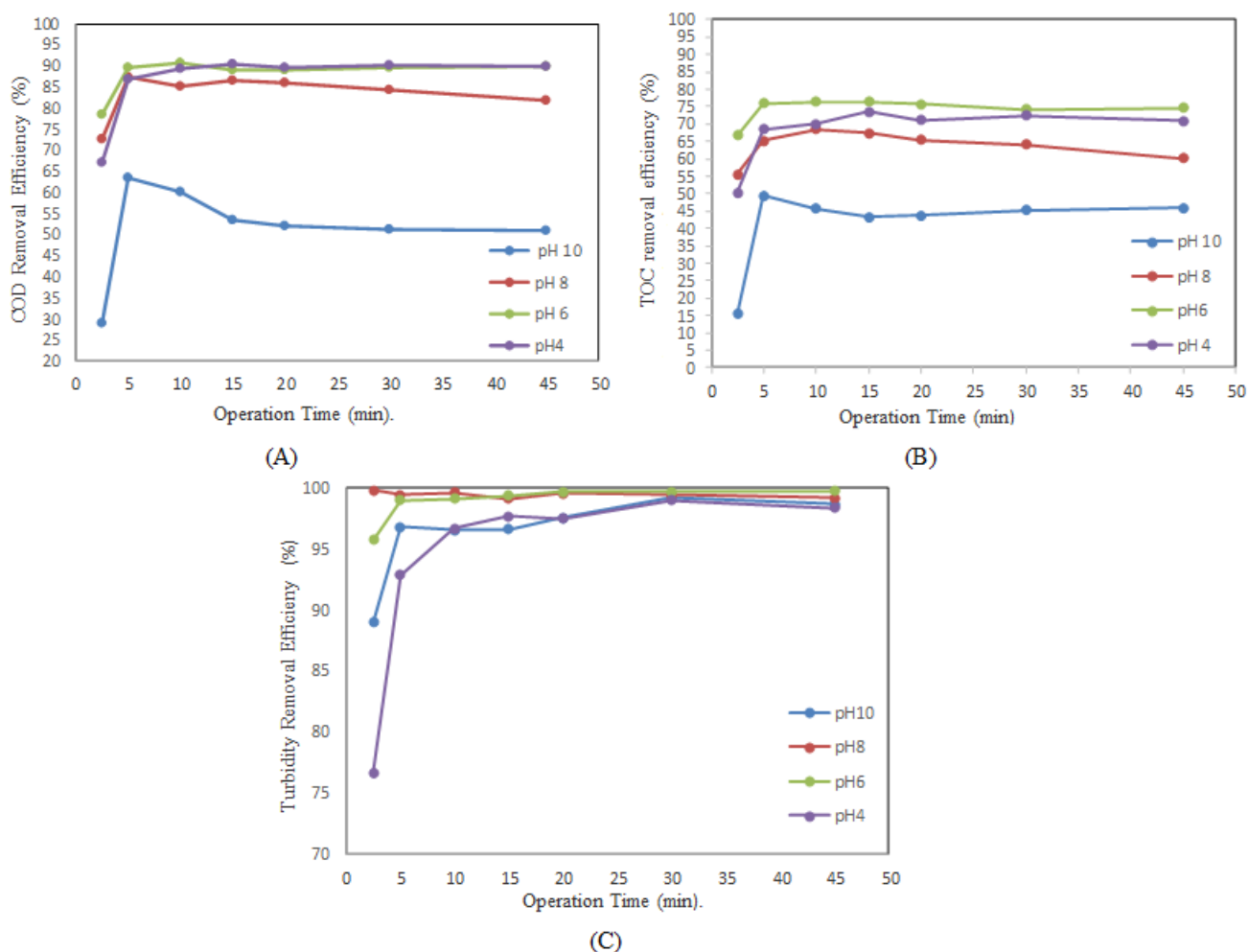


Figure 4. Effect of initial pH on removal efficiency for COD (A), TOC (B) and turbidity (C) (Operating conditions: Fe-Al-Fe-Al hybrid electrode, current density = 75 A/m^2 , air injection flow = 2 L/min , electrode surface area = 210 cm^2 and electrode connections mode = MP-P).

3.3 Effect of current density

Another important parameter in the electrochemical process is current density. The current density controls the reaction rate and specifies coagulant dosage within the electrochemical processes [43]. Moreover, bubble production and its size was adjusted and effected the growth of flocs by the current density. To determine the effect of current density for COD, TOC and turbidity removal, experiments were carried out at current densities ranged between $25\text{-}150 \text{ A/m}^2$.

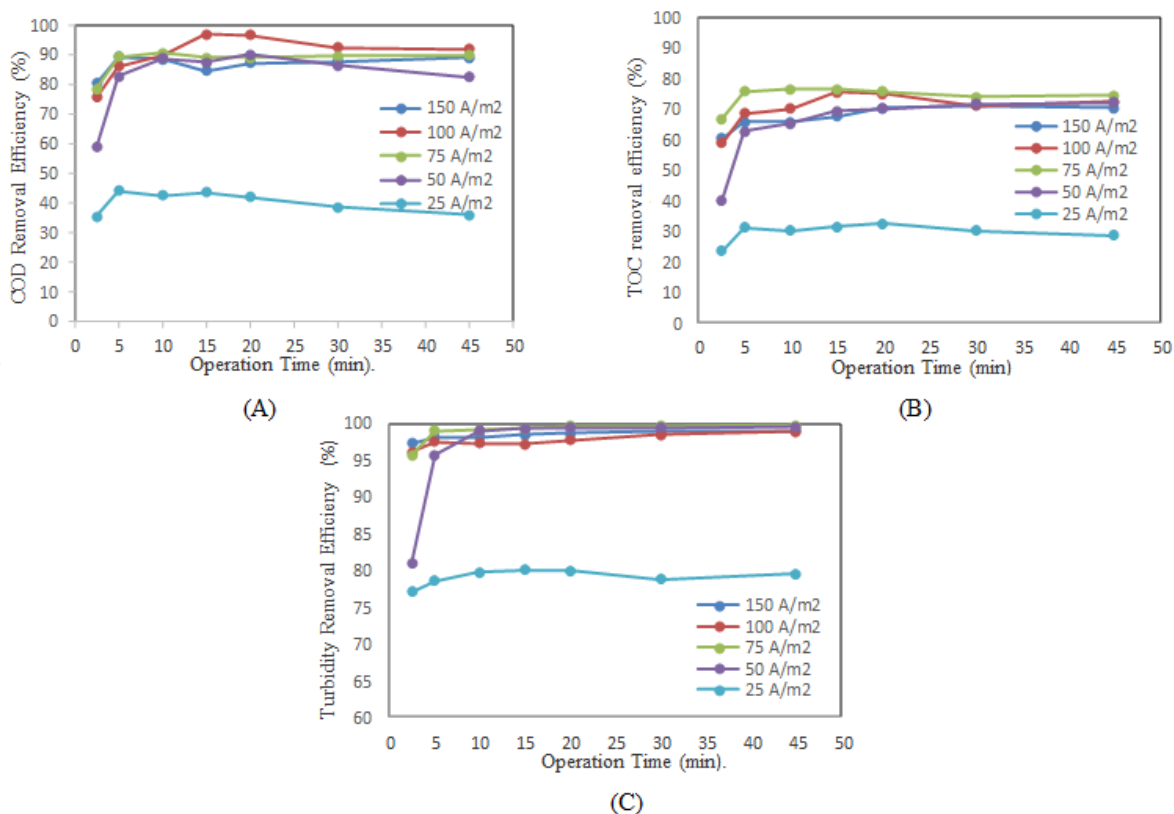


Figure 5. Effect of current density on removal efficiency for COD (A), TOC (B) and turbidity (C) (Operating conditions: Fe-Al-Fe-Al hybrid electrode, initial pH = 6, air injection flow = 2 L/min, electrode surface area = 210 cm² and electrode connections mode = MP-P).

Figure 5(A, B, C) shows the removal efficiencies for COD, TOC and turbidity as a function of the operating time at different current density values. The removal efficiencies for COD at 5 min were obtained as 44.1% at 25 A/m², 82.88% at 50 A/m², 89.5% at 75 A/m², 86.8% at 100 A/m², 89.3% at 150 A/m². As seen in Figure 5, the removal efficiency for COD increased with increasing current densities. Such a can be attributed to high current densities and increased metal hydroxide flocs with the extent of anodic dissolution. According to Faraday’s law, the amount of the metal electrode dissolved is straight the charge or current passed to the solution [37]. Thus, the metal hydroxide complexes formed may manage the removal of pollutants. Consequently, the removal efficiency for COD, TOC and turbidity increased with increasing current density levels. Gilpavas et al [21] found that current density in the study of treatability of automotive industry oily wastewater by electrocoagulation process using iron electrode was obtained as 4.3 mA/cm². When their study compared in this study (75A/m²), the optimum current density was obtained to higher than their study. This may be explained with more contain pollutants using the wastewater. The operation costs in 5 min were calculated as 0.15 \$/m³ at 25 A/m², 0.18 \$/m³ at 50 A/m², 0.24 \$/m³ at 75 A/m², 0.35\$/m³ at 100 A/m² and 0.66 \$/m³ at 100 A/m².

3.4 Effect of air injection flow

The effect of air injection flow on removal efficiencies for COD, TOC and turbidity were also investigated in present study. The experiments were carried out with air injection flow rates of between 0-6 L/min. The air not only increases oxidation of Fe^{+2}/Al^{+2} to Fe^{+3}/Al^{+3} but also provides the mixing or turbulence which promoted the coagulation/flocculation in the EC process [42]. The intension of dissolved oxygen in wastewater by air injection oxidized Fe^{+2}/Al^{+2} into Fe^{+3}/Al^{+3} which resulted in occurrence of $Me(OH)_3$ flocs. So, increased the removal efficiencies for COD, TOC and turbidity were observed with air injection. Kobya et al [43] and Parga et al [44] obtained satisfactory results with air injection in the EC process.

The effects of air injection flow on removal efficiencies for COD, TOC and turbidity were presented in Figure 6. As seen in Figure 6, the effects of air injection on removal efficiency for COD, TOC and turbidity were in positive direction. The removal efficiencies for COD, TOC and Turbidity without air injection were respectively obtained as 75.6%, 53.2% and 89.1% at 5 min. When the air injection flow rates were set as between 2-6 L/min, removal efficiencies for COD, TOC and turbidity increased respectively to 89.5%, 79.5% and 98.9% at 2 L/min air injection flow rate and respectively to 86.5 % (COD), 69.2% (TOC), 99.7% (turbidity) at 6 L/min air injection flow rate. In this study, air injection for removal of pollutants can be said to be beneficial.

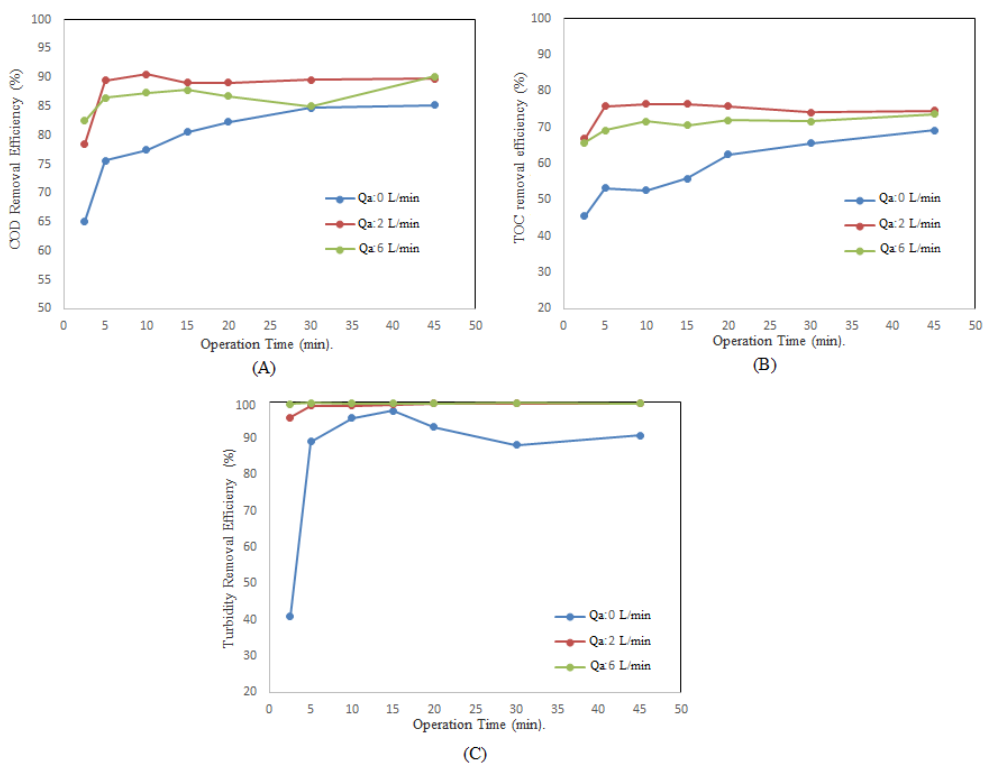


Figure 6. Effect of air injection flow on removal efficiency for COD (A), TOC (B) and turbidity (C) (Operating conditions: Fe-Al-Fe-Al hybrid electrode, initial pH = 6, current density = 75 A/m², electrode surface area = 210 cm² and electrode connections mode = MP-P).

3.5 Effect of electrode surface area

To investigate the effect of electrode surface area, experiments were carried out with the electrode surface areas of 210 cm², 420 cm² and 630 cm². The results are presented in Figure 7. As seen in Figure 7, electrode surface areas did not have significant effects on removal efficiencies for COD, TOC and turbidity. When the electrode surface areas were 210, 420 and 630 cm², the voltages respectively decreased to 19.7, 6.7 and 4.1 V. The removal efficiencies at 210, 420 and 630 cm² were respectively observed as 90.4, 84.6, 88.9 % for COD; as 75.9, 71.6, 76.9 % for TOC and as 98.9, 99.6, 99.2 % for turbidity. Values of current densities were calculated as 75 (210cm²), 37.5 (420cm²) and 25 (630cm²) A/m² at constant current of 1.57 A. Kobya et al [43] obtained to optimum electrode surface area 210 cm². Similarly, they claimed that the effect of electrode surface area on the removal of arsenic in this study was not important. As a result, any significant improvements were not observed in removal of pollutants with changing electrode surface areas. On the other hand, operating costs with respect to electrode surface area at 5 min were calculated as 0.24 (210 cm²), 0.12 (420 cm²) and 0.1 (630cm²) \$/m³.

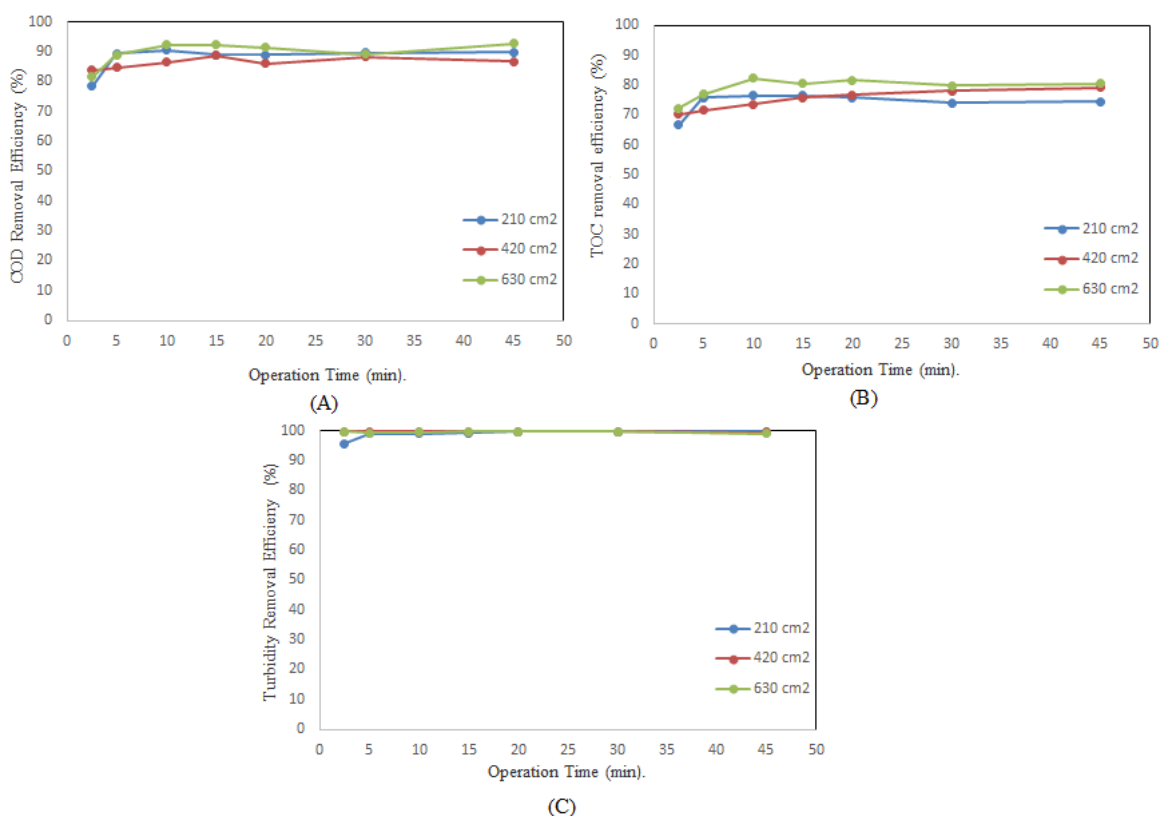


Figure 7. Effect of electrode surface area on removal efficiency for COD (A), TOC (B) and turbidity(C) (Operating conditions: Fe-Al-Fe-Al hybrid electrode, initial pH = 6, current density = 75 A/m², air injection flow = 2 L/min and electrode connections mode = MP-P).

3.6 Effect of electrode connection mode

The electrode connection mode is another important parameter on the removal of pollutants by the EC process. Effect of different electrode connection modes for the treatment of various wastewater was investigated by researchers [38, 45, 46]. To investigate the effects of different electrode connection modes on pollutant removal, three electrode connection modes were experimented. The hybrid electrodes were connected in MP-P, MP-S and BP-S connection modes (Figure 8) [19, 45, 46]. The effects of different electrode connection modes were shown in Figure 9. As seen in Figure 9, MP-S connection mode yielded higher removal efficiency for COD than the other connection modes. For the other performance parameters, the differences in removal efficiencies of electrode connection modes for TOC and turbidity were not significantly different from each other. The highest removal efficiencies for COD, TOC and turbidity were obtained with MP-S connection mode respectively as 94.5%, 79.5% and 98.5%. Kobya et al [38] found that the highest removal of Arsenic by EC process obtained to MP-S electrode connection mode in their study. In addition, the other researchers at the MP-S electrode connection mode in EC process obtained highest removal efficiencies than other electrode connection mode [45, 46]. Table 2 presents the removal efficiencies and operating costs of different connection modes.

Table 2. Results of removal efficiencies and operating costs at different connection modes and operation times.

	Operation Time (min.)						
	2.5	5	10	15	20	30	45
MP-P							
COD (% removal)	78.5	89.5	90.6	89.0	89.0	89.5	89.8
TOC (% removal)	66.8	75.9	76.5	76.5	75.8	74.1	74.6
Turbidity (% removal)	95.7	98.9	99.1	99.3	99.6	99.6	99.7
Operation Cost (\$/m ³)	0.12	0.24	0.48	0.72	0.97	1.43	2.11
Sludge production (kg/m ³)	0.54	0.65	0.93	1.19	1.51	1.95	2.66
MP-S							
COD (% removal)	82.5	94.5	95.6	95	94.5	94.2	90.5
TOC (% removal)	70.2	79.5	81.2	81.0	82.0	80.2	81.2
Turbidity (% removal)	96.8	98.5	99	99.5	99.4	99.01	99.4
Operation Cost (\$/m ³)	0.31	0.6	0.86	1.24	1.96	3.25	4.28
Sludge production (kg/m ³)	0,51	0,59	0,85	1,05	1,41	1,74	2,42
BP-S							
COD (% removal)	80.2	92.6	93.5	95.0	92.0	93.0	90.5
TOC (% removal)	68.5	78.2	80.2	81.0	82.0	81.0	82.0
Turbidity (% removal)	96.0	98.4	99.5	99.5	99.4	99	99.4
Operation Cost (\$/m ³)	0.28	0.54	0.76	1.15	1.56	2.56	3.84
Sludge production (kg/m ³)	0,48	0,55	0,81	1,06	1,47	1,80	2,58

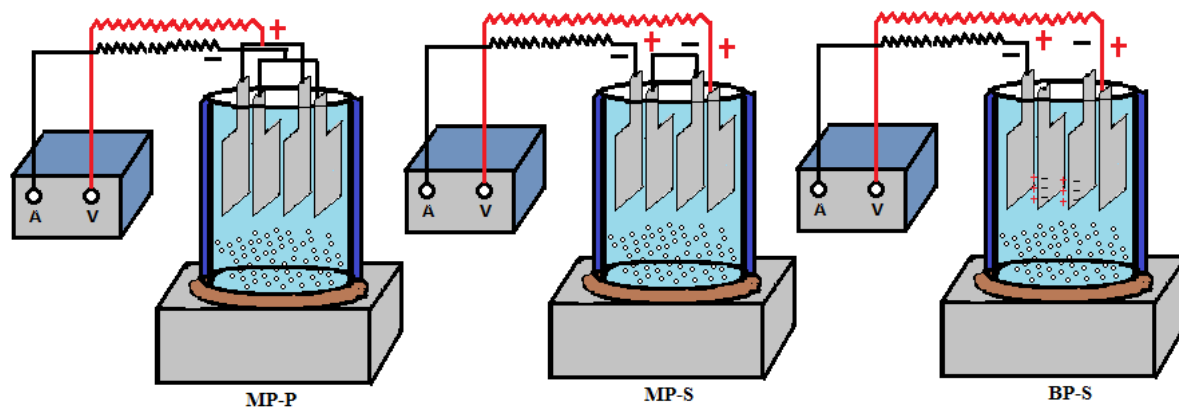


Figure 8. Schematic diagram of three different electrode connection modes in the EC process [19].

The operating costs at 5 min operating time were calculated as 0.24 \$/m³ at MP-P, 0.6 \$/m³ at MP-S and 0.54 \$/m³ at BP-S. Similarly, the other researchers found to be more expensive operation cost at MP-S electrode connection mode [45, 46]. The reason for the highest operating costs at series connection mode can be explained by higher potential in this mode than the parallel connection modes. Especially, electric consumption increases because the electrodes spend more voltage. Operation cost of MP-S connection mode was higher than the cost of other connection modes.

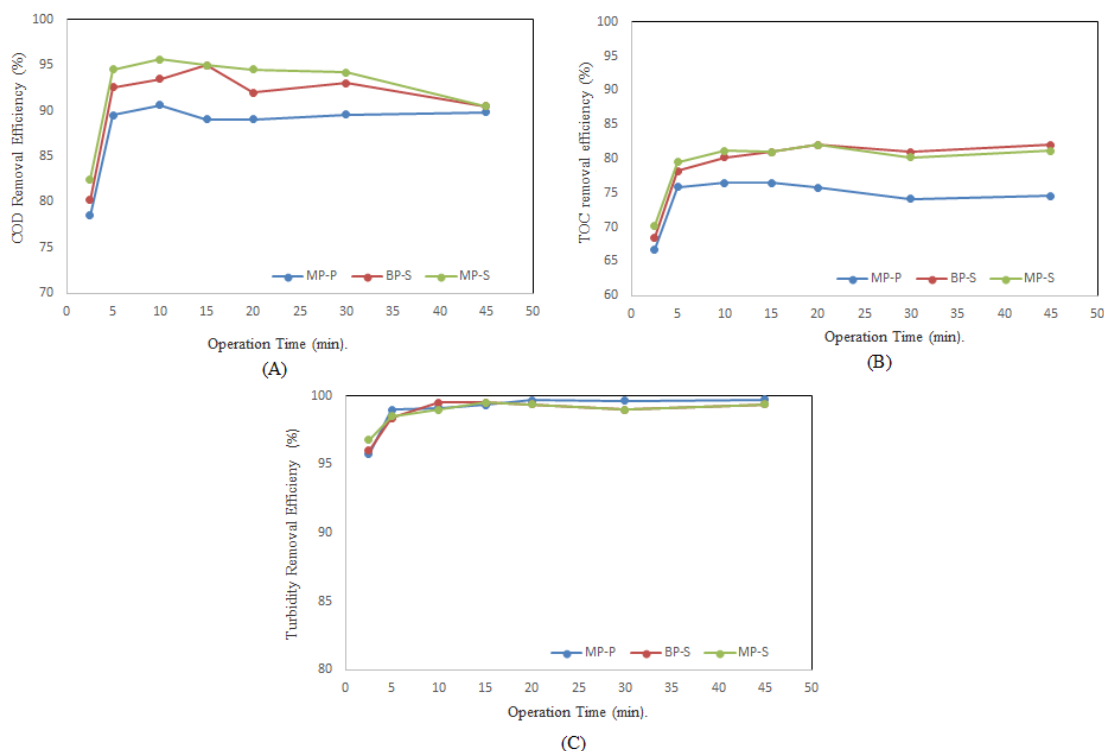


Figure 9. Effect of electrode connection mode on removal efficiency for COD (A), TOC (B) and turbidity(C) (Operating conditions: Fe-Al-Fe-Al hybrid electrode, initial pH = 6, current density = 75 A/m², air injection flow = 2 L/min and electrode surface area = 210 cm²).

In the EC process, pollutions were separated and floated in the form of sludge. So, the sludge production was important. As seen in Table 2, amount of the sludge produced in EC process changed for different electrode connection modes. Especially, the removal efficiencies of COD, TOC and turbidity increased with increasing the amount of sludge produced. This can be explained that, pollutants were effectively removed from the wastewater by adsorption and coprecipitation on metallic sludge. The lowest of the amount of sludge produced at 5 min operation time was obtained as 0.55 kg/m^3 for BP-S. The highest of removal efficiencies of pollutants at 10 min. and electrode connection mode MP-S in EC process was 0.85 kg/m^3 . Under optimum operating conditions, the amount of sludge produced was found to be 0.59 kg/m^3 .

4. CONCLUSIONS

The removal efficiencies for COD, TOC and turbidity from oily wastewater of train industry were investigated in this study by using hybrid iron and aluminum electrodes at different connection modes in a batch reactor. Different operating parameters such as the type of electrode pairs, initial pH, current density, air injection flow, electrode surface area, electrode connection modes and operation time were experimented to determine the optimum conditions for the highest removal efficiencies for COD, TOC and turbidity. Hybrid electrode pairs have significant effects on pollutant removal efficiencies. The highest removal efficiencies of COD and TOC were obtained from Fe-Al-Fe-Al electrode pairs at 5 min operating time. For turbidity, removal efficiency of all electrode pairs were quite close to each other. Electrode connection mode was identified as another significant parameter in pollutant removal. The highest removal efficiencies of COD and TOC were observed in MP-S connection mode. Thus, the effects of hybrid electrode pairs and electrode connection modes on removal efficiencies for COD, TOC and turbidity were found to be significant. The removal efficiencies of COD, TOC and turbidity at optimum operating conditions (Fe-Al-Fe-Al electrode pairs, initial pH of 6, current density of 75 A/m^2 , air injection flow of 2 L/min. , electrode surface area of 210 cm^2 and electrode connection mode of MP-S) were respectively obtained as 94.5%, 79.5% and 98.5%. Satisfactory results were achieved especially in a short operation time (at 5 min). Operating costs of different electrode connection modes for operation times of 5-45 min ranged between $0.12\text{-}2.11 \text{ \$/m}^3$ at MP-P, between $0.31\text{-}4.28 \text{ \$/m}^3$ at MP-S and between $0.28\text{-}3.84 \text{ \$/m}^3$ at BP-S. Under optimum operating conditions, the operating cost was $0.60 \text{ \$/m}^3$. It was concluded in this study that EC process with iron and aluminum hybrid electrode pairs were quite efficient and cost-effective in treatment of oily wastewater effluent of parts washing machine of train industry.

ACKNOWLEDGEMENTS

This project was funded by the Cumhuriyet University Research Foundation (Project Code: M-521). The author, therefore, acknowledge with thanks Cumhuriyet University Research Foundation technical and financial support.

References

1. M. Tir, N. Moulai-Mostefa, *J. Hazard. Mater.*, 158 (2008) 107.
2. E. Gilpavas, K. Molina-Tirado, M. Gomez-Garcia, *Water Sci. Tech.*, 60 (2009) 2581.
3. A.I. Zouboulis, A. Avranas, *Coll. Surf. A* 172 (2000) 153.
4. K. Scott, R.J. Jachuck, D. Hall, *Sep. Purif. Technol.*, 22 (2001) 431.
5. N. Moulai-Mostefa, A. Brou, L. Ding, M.Y. Joffrin, *Mec. Ind.*, 6 (2005) 203.
6. G. Rios, C. Pazos, J. Coca, *Coll. Surf. A* 138 (1998) 383.
7. Z.S. Lin, W. Wen, *Mar. Environ. Sci.*, 22 (2003) 15.
8. Y.B. Zeng, C.Z. Yang, J.D. Zhang, W.H. Pu, *J. Hazard. Mater.*, 147 (2007) 991.
9. T. Wang, *Oil-Gasfield Surf. Eng.*, 26 (2007) 26.
10. A.A. Al-Shamrani, A. Jamesa, H. Xiao, *Coll. Surf.*, A 209 (2002) 15.
11. G.H. Liu, Z.F. Ye, K. Tong, Y.H. Zhang, *Biochem. Eng. J.*, 72 (2013) 48.
12. X. Zhao, Y.M. Wang, Z.F. Ye, A.G.L. Borthwick, J.R. Ni, *Process Biochem.*, 41 (2006) 1475.
13. S. E. Burns, S. Yiacoumi, C. Tsouris, *Sep. Purif. Technol.*, 16 (1999) 193.
14. X. Chen, G. Chen, P. L. Yue, *Environ. Sci. Technol.*, 36 (2002) 778.
15. C. L. Lai, S. H. Lin, *Chemosphere* 54 (2004) 235.
16. C.L. Yang, *Sep. Purif. Technol.*, 54 (2007) 388.
17. M.R.G. Santos, M.O.F. Goulart, J. Tonholo, C.L.P.S. Zanta, *Chemosphere*, 64 (2006) 393.
18. H.Z. Ma, B. Wang, *J. Hazard. Mater.*, 132 (2006) 237.
19. M.Y.A. Mollah, R. Schennach, J.P. Parga, D.L. Cocke, *J. Hazard. Mater.*, 84 (2001) 29.
20. M. Bayramoglu, M. Kobya, M. Eyvaz, E. Senturk, *Sep. Purif. Technol.*, 51 (2006) 404.
21. A. Dalvand, M. Gholami, A. Joneidi, N.M. Mahmoodi, *Clean-Soil Air Water*, 39 (2011) 665.
22. G. Chen, *J. Environ. Eng.* 126 (2000) 858.
23. M. Kobya, M. Bayramoglu, M. Eyvaz, *J. Hazard. Mater.*, 148 (2007) 311.
24. M. Kobya, H. Hiz, E. Senturk, C. Aydiner, E. Demirbas, *Desalination*, 190 (2006) 201.
25. X. Chen, G. Chen, P.L. Yue, *Sep. Purif. Technol.*, 19 (2000) 65.
26. M. Kobya, E. Senturk, M. Bayramoglu, *J. Hazard. Mater.*, 133 (2006) 172.
27. O.Y. Pykhiteev, A.A. Ofimou, L.N. Moskvina, *Russ. J. Appl. Chem.*, 72 (1999) 9.
28. M. Rebhun, M. Lurie, *Water Sci. Technol.*, 27 (1993) 1.
29. G. Chen, *Sep. Purif. Technol.*, 38 (2004) 11.
30. Y.O. Fouad, *Alexandria Engineer. J.*, 53 (2014) 199.
31. X. Xu, X. Zhu, *Chemosphere*, 56 (2004) 889.
32. K. Ulucan, U. Kurt, *J. Elect. Chem.*, 747 (2015) 104.
33. C-L. Yang, *Separ. Purif. Technol.*, 54 (2007) 388.
34. APHA, AWWA, WEF, Standard methods for examination of water and wastewater, twentieth ed., American Public Health Association, Washington, DC, 1992.
35. P.R. Kumar, S. Chaudhari, K.C. Khilar, S.P. Mahajan, *Chemosphere*, 55 (2004) 1245.
36. F. Akbal, S. Camci, *Environ. Prog. Sustain. Energy.*, 31(2012) 341.
37. M. Kobya, A. Akyol, E. Demirbas, M.S. Oncel, *Environ. Prog. Sustain. Energy.*, 33 (2013) 131.
38. M. Kobya, F. Ulu, U. Gebologlu, E. Demirbas, M.S. Oncel, *Sep. Purif. Technol.*, 77 (2011) 283.
39. M. Kobya, U. Gebologlu, F. Ulu, M.S. Oncel, E. Demirbas, *Electrochim. Acta.*, 56 (2011) 5060.
40. F. Ozyonar, B. Karagoz, *Desalination and Water Treat.*, 52 (2014) 74.
41. M. Asselin, P. Drogui, H. Benmoussa, J.F. Blais, *Chemosphere*, 72 (2008) 1727.
42. N. Modirshahla, M.A. Behnajady, S. Kooshaiian, *Dyes Pigments*, 74 (2007) 249.
43. M. Kobya, F. Ozyonar, E. Demirbas, E. Sik, M.S. Oncel, *J. Environ. Chem. Engineer.*, 3 (2015) 1096.
44. J.R. Parga, D.L. Cocke, V. Valderde, J.A.G. Gomes, M. Kesmez, H. Moreno, M. Weir, D. Mencer, *Chem. Eng. Technol.*, 28 (2005) 605.
45. Y. Demirci, L.C. Pekel, M. Alpbaz, *Int. J. Electrochem. Sci.*, 10 (2015) 2685.

46. A.S. Naje, S. Chellipan, Z. Zakaria, S.A. Abbas, *Int. J. Electrochem. Sci.*, 10 (2015) 5924.

© 2016 The Authors. Published by ESG (www.electrochemsci.org). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).