

Electrocoagulation for COD and diesel removal from oily wastewater

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Abstract This study investigated the diesel and COD removal from oily wastewater by electrocoagulation. Experiments were conducted in a 2-l reactor using aluminum and iron electrodes. Effects of different parameters including pH (3–11), time (10–60 min), voltage (4.5–10.5 V), supporting electrolyte (NaCl concentration), electrode material and initial diesel concentration (3500–11,000 mg/L) were studied in order to evaluate the efficiency of electrocoagulation. Furthermore, the consumption of energy and the amount of sludge produced by this method were evaluated. The highest removal efficiency (COD removal of $99.1 \pm 0.2\%$ and diesel removal of $98.8 \pm 0.2\%$) was observed under the following conditions: pH 7, 40 min, 10.5 V, NaCl concentration of 0.5 g/L, diesel concentration of 3500 mg/L. The consumption of energy was estimated to be 6.47 kWh/m³, and the amount of sludge generated was 1995 mg/L. The results demonstrated that the electrocoagulation is a feasible technique for treatment of heavily contaminated petroleum refinery wastewater.

Keywords COD removal · Diesel removal · Electrocoagulation · GC–MS · Oily wastewater

Introduction

Petroleum refineries' wastewater

Large quantity of water is used by petroleum refineries for different objectives such as distillation, hydrotreating, desalting and cooling systems (Yavuz et al. 2010); hence, they create considerable quantities of wastewater. The features of the generated wastewater depend strongly on the process configuration (Rasheed et al. 2011).

Petroleum refineries' wastewater has high concentrations of aliphatic and aromatic petroleum hydrocarbons (El-Naas et al. 2009; Sun et al. 2008). Refinery effluents possess contaminants such as cyanide, oil, phenols, benzene, sulfide, ammonia and heavy metals. This wastewater is normally rich in biological oxygen demand (BOD) and chemical oxygen demand (COD) (Rasheed et al. 2011; Verma et al. 2013), which usually have damaging and harmful effects on plants, sea, river as well as surface and groundwater sources (El-Naas et al. 2009; Sun et al. 2008). Facilities are required to reduce the concentration of organic contaminants in their wastewater to a value susceptible to microbial degradation prior to the final biological treatment and purification stage. These pretreatment units are normally consisting of ultrafiltration, adsorption, coagulant and coagulant aides and electrochemical processes (El-Naas et al. 2009).

Electrocoagulation

Electrocoagulation (EC) is one of the novel methods for water and wastewater treatment (Chafi et al. 2011). The EC process possesses several advantages such as easy operation, short treatment time, low sludge production and no chemical requirement (Gengec et al. 2012). The EC is a technology

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that has been effectively used to treat industrial wastewater containing different pollutants such as arsenic, phosphate, boron, dyes and viruses. Furthermore, it has been effective in breaking oil emulsions in water and treating paper mill effluent, olive mill effluent, landfill leachate and dairy effluent (Bensadok et al. 2008; Irdemez et al. 2006; Katal and Pahlavanzadeh 2011; Khoufi et al. 2007; Li et al. 2011; Azadi Aghdam et al. 2015; Phalakornkule et al. 2010; Sengil and Ozacar 2006; Tchamango et al. 2010; Wan et al. 2011; Yilmaz et al. 2008; Zhu et al. 2005; Amani-Ghadim et al. 2013).

Few studies have investigated the removal of hydrocarbons using EC process. Moussavi et al. (2011) used EC process for removing hydrocarbons from contaminated groundwater. Effects of pH, electrode material, current density and treatment time are investigated, and the removal efficiency of 95.1 % for total hydrocarbon was achieved in optimized conditions (pH of neutral, electrode arrangement of steel–aluminum as anode–cathode and current density of 18 mA/cm²). Karhu et al. (2012) studied bench-scale treatment of 0.6 and 2 % bio oil-in-water and synthetic oil-in-water emulsions. No significant difference was detected in using stainless steel or aluminum electrodes. Furthermore, turbidity, COD and TOC removals of 75–100, 25–95 and 20–75 % were achieved, respectively.

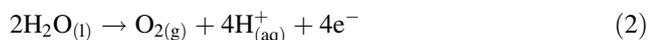
In an EC process, the coagulating ions are generated in situ involving three stages (a) electrolytic reactions at electrode surfaces, (b) formation of coagulants in aqueous phase and (c) adsorption of soluble or colloidal pollutants on coagulants, which are removed by sedimentation or flotation (Kobyta et al. 2003). Iron (Fe) and aluminum (Al) have been extensively applied as a sacrificial electrode in the EC process (Gengec et al. 2012, Kobyta et al. 2006). Sacrificial electrode dissolves from the anode creating corresponding metal ions. These ions hydrolyze to polymeric iron or aluminum oxyhydroxides, which are the coagulating agents (Gengec et al. 2012).

Reactions and mechanisms

The major reaction at the anode when aluminum electrode is applied in the EC process is as follows:



In addition, oxygen evolution can compete with aluminum dissolution at the anode by the following reaction:



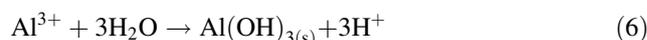
At the cathode, hydrogen evolution occurs by the following reaction. It contributes to floatation of the flocculated particles to the surface of the wastewater.



At high pH values, generated OH[−] at the cathode attacks the cathode by the following reaction (Gengec et al. 2012; Kobyta et al. 2003, 2006):



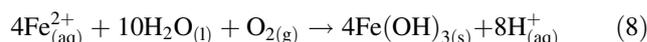
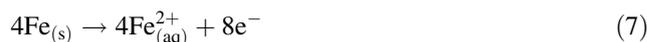
Electrode reactions generate Al_(aq)³⁺ and hydroxyl ions [Reactions (1) and (4)] to form different monomeric–polymeric species such as Al(OH)₄[−], Al₁₃(OH)₃₄⁵⁺, Al₇(OH)₁₇⁴⁺, Al₈(OH)₂₀⁴⁺, Al₂(OH)₂⁴⁺, Al(OH)₂²⁺, Al(OH)₂⁺, Al₁₃O₄(OH)₂₄⁷⁺, Al₆(OH)₁₅³⁺ which transform primarily into Al(OH)_{3(s)} and eventually polymerize to Al_n(OH)_{3n} [Reactions (5) and (6)] in the solution (Gengec et al. 2012; Kobyta et al. 2006):



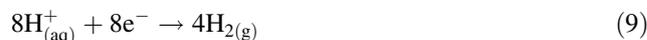
Formed amorphous Al(OH)_{3(s)} have great surface areas and contribute to quick adsorption of soluble organic compounds and also trapping the colloidal particles which are easily separated from aqueous medium by H₂ floatation or sedimentation (Kobyta et al. 2006). The concentration of hydrolyzed aluminum species relies on the pH and aluminum concentration (Gengec et al. 2012).

Iron produces Fe(OH)_n where *n* = 2 or 3 upon oxidation in an electrolytic system. Two mechanisms have been suggested for the formation of Fe(OH)_n (Gendel and Lahav 2010; Mollah et al. 2001). The first mechanism includes the reactions (7)–(10):

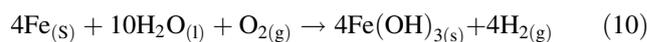
At the anode:



At the cathode:

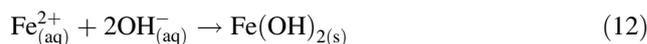


Overall:



The second mechanism includes the reactions (11)–(14):

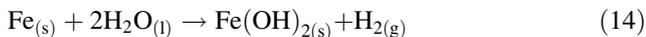
At the anode:



At the cathode:



Overall:



Fe^{2+} and Fe^{3+} ions will immediately undergo further spontaneous reactions to create monomeric ions, ferric hydroxo complexes with hydroxide ions and polymeric species such as $\text{Fe}(\text{OH})_2^{4+}$, $\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{OH})_2^{2+}$, $\text{Fe}(\text{OH})_4^-$, $\text{Fe}(\text{H}_2\text{O})_2^+$, $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$, $\text{Fe}(\text{H}_2\text{O})_8(\text{OH})_2^{4+}$, $\text{Fe}_2(\text{H}_2\text{O})_6(\text{OH})_4^{2+}$, $\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2^+$, $\text{Fe}(\text{OH})_3$ depending on the pH of the wastewater (Akyol 2012, Zaided and Bellakhal 2009). The formed gelatinous suspension of $\text{Fe}(\text{OH})_{n(s)}$ that remains in the aqueous medium removes the waste matter from wastewater either by complex formation or by electrostatic attraction, followed by coagulation (Mollah et al. 2001).

In the present research that have been conducted throughout 2013 at Sharif University of Technology, Tehran, Iran, the effect of different parameters including pH, time, voltage, supporting electrolyte, electrode material and initial diesel concentration on diesel and COD removal by EC was studied. Evaluation of all parameters which may affect the process was the primary aim of this research besides presenting and discussing sludge production and energy consumption data in order to achieve maximum potential of this process.

Materials and methods

In this study, synthetic wastewater was made and used in the EC setup (Fig. 1) by polluting water with different concentrations of diesel. The EC treatment was performed in a batch electrolytic reactor made from Plexiglas material. The EC cell consisted of three aluminum electrodes

and three iron electrodes as cathodes and anodes. Total effective surface area of the electrodes was $6 \times 8 \times 10 \text{ cm}^2$, and distance between each pair of electrodes was 2 cm.

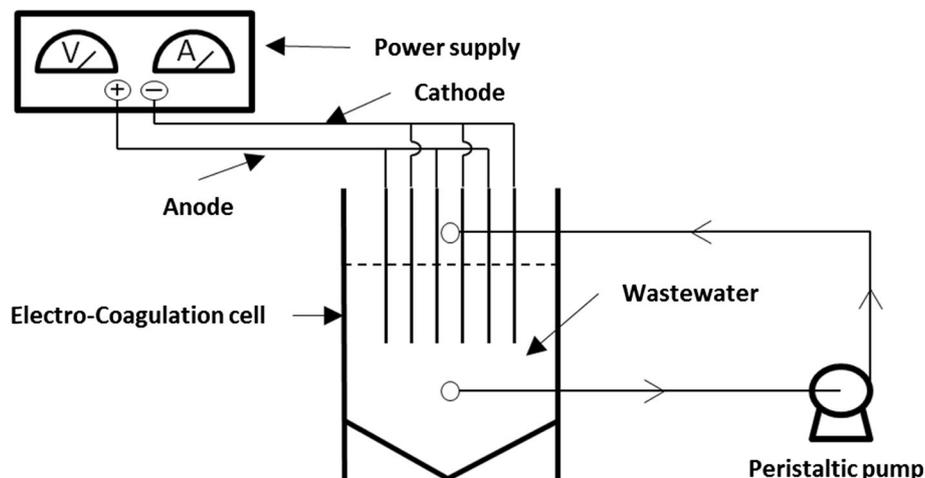
The EC cell was connected in monopolar parallel connection mode. In each run, 2 l of wastewater was placed inside the EC reactor. Wastewater was mixed by a peristaltic pump (Heidolph, Germany), and the current density was adjusted by a digital DC power supply (IMV Corporation, Japan) operated at galvanostatic mode. Before each run, electrodes were washed by HCl solutions (35 %) and hexamethylenetetramine (2.8 %) to remove the oxide and passivation layers from the electrodes (Gengec et al. 2012). HCl solution (0.1 N) and NaOH solution (0.1 N) were used to adjust pH. NaCl was used as an electrolyte, and all experiments were performed at room temperature (25 °C).

Samples were filtered after the experiment by a 1.6- μm Whatman glass microfiber filter and then were analyzed. The initial and final COD concentrations were measured according to standard methods 5220D (Clesceri and Eaton 1998).

At the end of each EC experiment, the amount of formed sludge (metal hydroxide flocs together with removed pollutants) was determined by means of the total suspended solid measurements according to standard methods 2540D (Clesceri and Eaton 1998).

Diesel concentration was measured using UV–Vis spectrophotometry method, which previously used in Joint Danube Survey (2002). The only difference between current method and cited method is in measuring the UV absorbance using Unico-UV-2100 spectrophotometer at wavelength of 250 nm instead of 254 nm due to its highest absorbance among other wavelengths ranging from 220 to 300 nm. In addition, diesel concentration and type of hydrocarbons were determined by GC–MS (Agilent Technologies-7890). The pH and conductivity of samples

Fig. 1 Schematic diagram of the EC cell



were measured using pH meter (HANNA pH 211) and conductometer (HACH-Sension7), respectively. All materials used were products of Merck Co., Germany.

Removal efficiency of the wastewater treated by EC was computed as follows:

$$\text{Removal efficiency} = \frac{C_0 - C_e}{C_0} \times 100 \quad (15)$$

where C_0 is the initial concentration (mg/L) and C_e stands for concentration at any time (mg/L).

One of the most significant parameters that affect the application of any method of wastewater treatment is the cost. The operating cost in the EC process includes material (mainly electrode material), consumption of energy costs, labor, maintenance, sludge dewatering and disposal and fixed costs (Kobyta et al. 2006). Consumption of energy cost is the major cost in the EC process; hence, this item was calculated. Consumption of energy (kWh/m³) was calculated using the following equation:

$$\text{Energy Consumption (kWh/m}^3\text{)} = \frac{V \cdot I \cdot t}{\text{Treated volume}(l)} \quad (16)$$

where V is assigned as the cell voltage (V), I is the current (A) and t represents the operating time (h).

The resistance on the electrode varies throughout the experiments. In order to achieve accurate results, current was monitored and weighted average of that is used for the calculations.

Results and discussion

The effect of several parameters including pH, reaction time, voltage, electrode material, supporting electrolyte and the initial diesel concentration on the performance of EC in removing COD and diesel from synthetic wastewater was investigated. Also, the consumption of energy and the amount of sludge produced by this method were presented. The results are demonstrated and discussed below.

Effect of pH on electrocoagulation

The effect of pH on the removal efficiency of COD and diesel was investigated and is shown in Fig. 2a. It can be seen that the initial pH has a significant impact on the COD and diesel removal efficiency. The maximum removal efficiency of COD and diesel was observed at pH around 7. The removal efficiency of the COD and diesel in this pH region was 57.9 ± 2.0 and 52.1 ± 1.5 %, respectively.

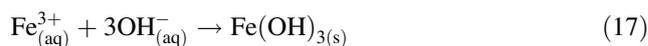
During the EC process, a pH increase is observed when the initial pH is acidic. The interpretation for this

phenomenon is that this increase is due to the release of over-saturated CO₂ because of hydrogen evolution at cathodes (Bazrafshan 2008; Chen et al. 2000; Kobyta et al. 2006). It is also found that in the alkaline mediums, pH of the solution decreases through the treatment, which is due to precipitation of hydroxide ions with cations. These results show that EC can act as pH buffer.

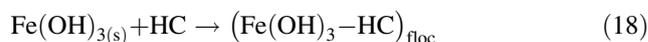
The COD and diesel removal efficiencies decreased in acidic and alkaline conditions. This result can be explained by the distribution of iron ionic species. The species are useful for removal of pollutants, which are stable and insoluble. According to predominance zone diagram for iron (III) (Barrera-Diaz et al. 2003), at acidic conditions the species of Fe³⁺, Fe(OH)₂⁺, Fe(OH)₂²⁺ ions are dominant and at alkaline condition Fe(OH)₄⁻ ion is dominant and these species are soluble; moreover, the solubility of Fe(OH)_{3(s)} increases and these species are not effective for removal of COD and diesel. However, in neutral pH, Fe(OH)_{3(s)} is stable, insoluble and available for pollutant adsorption from wastewater. Thus, Fe(OH)_{3(s)} has the major role in the removal of COD and diesel.

The constituents of hydrocarbon molecules are hydrophobic and nonpolar neutral; hence, they have probably been removed from the wastewater through the formation of surface complexes by gelatinous Fe(OH)_{3(s)} precipitate. The active sites on hydrocarbon molecules complex present the surfaces of ferric hydroxide flocs which are growing (co-precipitation) and undergo physical adsorption onto the amorphous Fe(OH)_{3(s)} flocs using van der Waals forces (Moussavi et al. 2011).

Based on the following reactions, the mechanism involved in the removal of petroleum hydrocarbons can be simplified (Moussavi et al. 2011): Formation of ferric hydroxide (at 6 < pH < 9):



Adsorption of hydrocarbons (HC):



(Fe(OH)₃-HC) flocs can attach together and flocculate; thus, contaminants are separated from the wastewater by settling, flotation or filtration (Moussavi et al. 2011). This is consistent with the findings of Farhadi, et al. (Farhadi et al. 2012).

The effect of pH on the amount of sludge produced and consumption of energy is shown in Fig. 2b. By increasing pH from 3 to 11, the amount of sludge formed increases from 448 to 496 mg/L and consumption of energy from 0.206 to 0.322 kWh/m³. Hence, at different initial pHs, sludge production and consumption of energy were nearly constant.

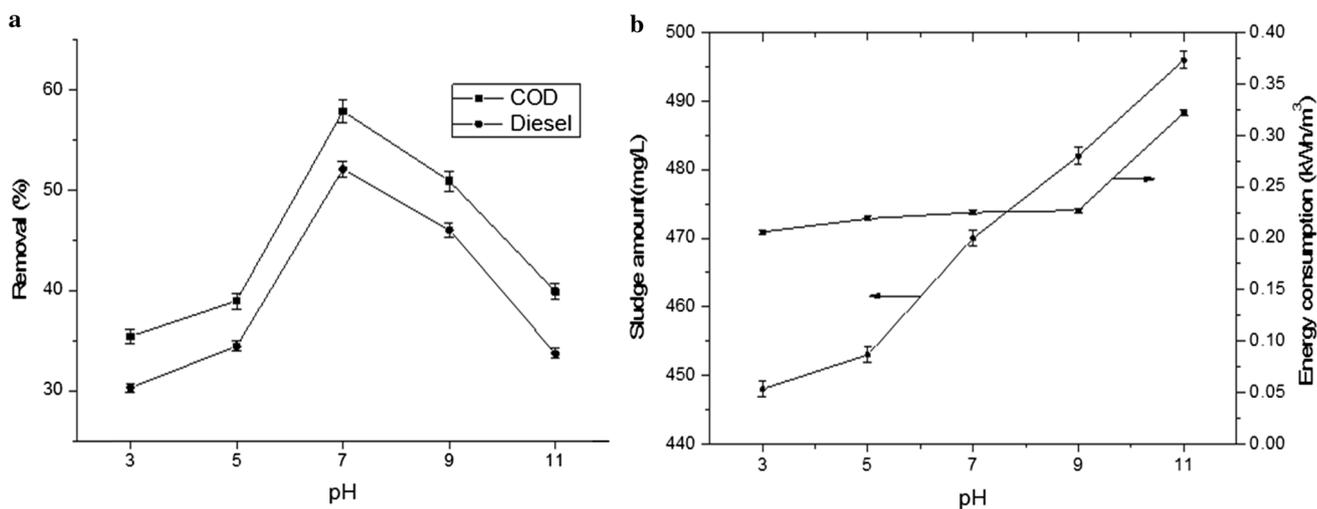


Fig. 2 a Effect of pH on the removal of COD and diesel and b effect of pH on the amount of sludge produced and consumption of energy (20 min, 4.5 V, NaCl concentration of 0.5 g/L, Fe-anode, Al-cathode, initial diesel concentration of 3500 mg/L)

Effect of time on electrocoagulation

The effect of time on the removal efficiency of COD and diesel in the EC process was investigated, and it is shown in Fig. 3a. The removal efficiencies of COD and diesel during the 60-min operation increased from 42.4 ± 3.0 to 85.0 ± 3.4 % and from 36.0 ± 2.0 to 82.03.0 %, respectively. The removal efficiencies of the COD and diesel were nearly constant after 40 min of operating time. The removal efficiencies of the COD and diesel after 40 min were 83.3 ± 2.3 and 78.3 ± 2.5 %, respectively.

Electrolysis time determines the rate of production of metal ions from electrodes. The COD and diesel removal efficiencies depend directly on the concentration of metal

ions produced by the electrodes. That subject is justifiable by Faraday’s law [Eq. (19)]. According to Faraday’s law, theoretically, the amount of coagulant is directly proportional to the applied current to the electrolytic cell and time.

$$C = \frac{Mit}{nFV} \tag{19}$$

where *M*, *I*, *t*, *n*, *F* and *V* stand for molecular weight of metal (g/mol), current (A), time (s), metal valence (3 for Al and 2 for Fe), Faraday constant (96,500 C/mol) and volume of wastewater, respectively (Kobyta et al. 2010).

At the beginning of the EC process, the COD and diesel removal efficiencies are low since at initial times, the rate

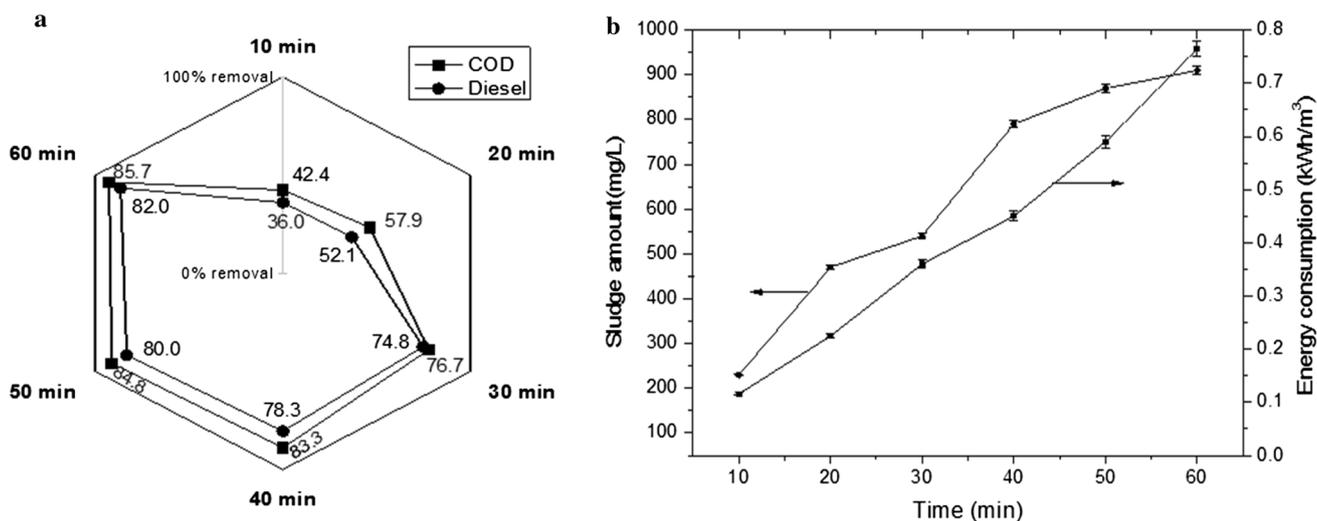


Fig. 3 a Effect of time on the removal of COD and diesel and b effect of time on the amount of sludge produced and consumption of energy (pH 7, 4.5 V, NaCl concentration of 0.5 g/L, Fe-anode, Al-cathode, initial diesel concentration of 3500 mg/L)

of production of metal ions from electrodes is low; however, when the electrolysis time increases, the concentration of metal ions and their hydroxide flocs increases; thus, the COD and diesel removal efficiencies increase. The removal efficiencies of the COD and diesel were nearly constant after 40 min of operating time since metal ions and their hydroxide flocs cover the electrode surface. Moreover, this has caused electrode passivation and the concentration of metal ions and their hydroxide flocs became constant; thus, the COD and diesel removal efficiencies did not change significantly. This is consistent with the findings of Chavalparit and Ongwandee (2009) that when operation time is increased, the removal efficiency is increased as well.

The effect of time on the amount of sludge produced and consumption of energy is shown in Fig. 3b. By increasing the time from 10 min to 60 min, the sludge formation rate from 230 to 910 mg/L and consumption of energy from 0.116 to 0.765 kWh/m³ are increased.

The results have shown that sludge production and consumption of energy were proportional to time. According to Faraday's law [Eq. (19)], the amount of metal hydroxide formation and coagulant are directly proportional to time; thus, by increasing time, the produced sludge is increased. Furthermore, according to Eq. (16), consumption of energy is directly proportional to time; thus, by increasing time, consumption of energy is increased. In addition, the amount of sludge produced and consumption of energy increase by increasing the COD and diesel removal.

Effect of voltage on electrocoagulation

The voltage applied to the EC system determines the coagulant dosage rate. The effect of voltage on the removal

efficiency of COD and diesel is shown in Fig. 4a. The removal efficiencies of COD and diesel are increased with the voltage (4.5–10.5 V) from 83.3 ± 2.30 to 96.9 ± 1.2 % and from 78.3 ± 2.5 to 96.8 ± 1.0 %, respectively.

The applied voltage is an important parameter for the COD and diesel removal since it determines the coagulant dosage rate, concentration of metal ions and their hydroxide flocs. When voltage increases, the concentration of metal ions and their hydroxide flocs increase to absorb hydrocarbons. That subject is justifiable by Faraday's law [Eq. (19)]. Thus, the COD and diesel removal efficiencies are increased.

In addition to decreasing bubble size, the bubble generation rate increases with the increasing of voltage, which is beneficial for pollutants removal (Farhadi et al. 2012; Li et al. 2011). Since this has caused that the contact between hydroxide flocs and pollutants increases, the flotation process is improved and pollutants are rapidly removed.

The effect of voltage on the amount of sludge produced and consumption of energy is shown in Fig. 4b. By increasing the voltage from 4.5 to 10.5 V, the sludge formation rate from 790 to 1930 mg/L and consumption of energy from 0.45 to 4.72 kWh/m³ are increased. The results have shown that sludge production and consumption of energy were proportional to voltage. According to Faraday's law [Eq. (19)], the amount of metal hydroxide formation and coagulant is directly proportional to voltage; thus, by increasing voltage, sludge produced is increased. According to Eq. (16), consumption of energy is directly proportional to voltage; thus, by increasing voltage, consumption of energy is increased. In addition, the amount of sludge produced and consumption of energy increase by increasing the COD and diesel removal.

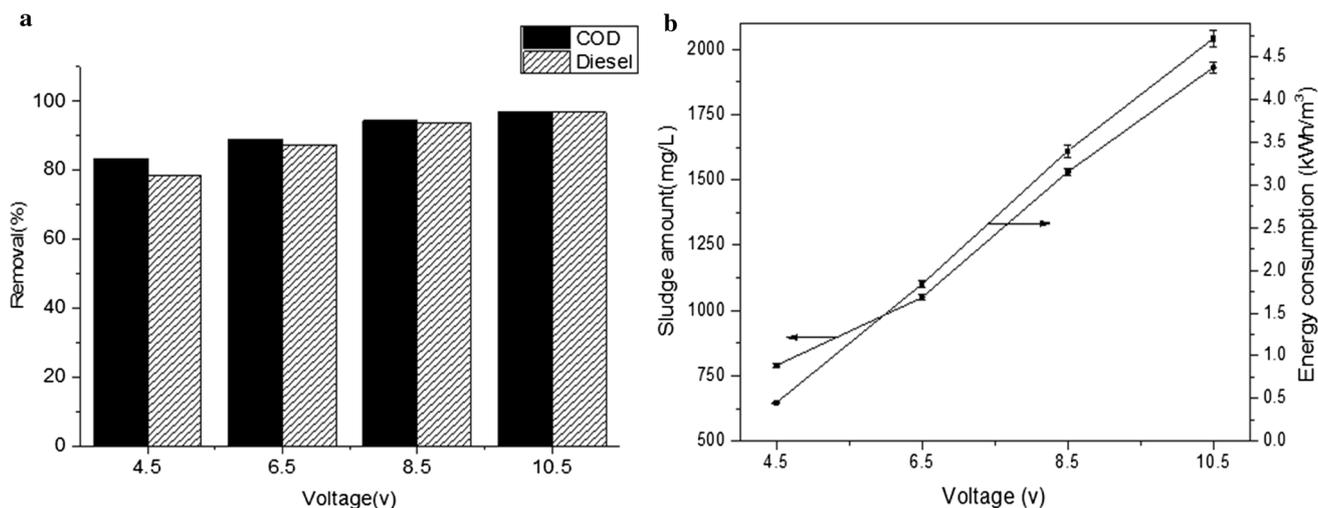


Fig. 4 **a** Effect of voltage on the removal of COD and diesel and **b** effect of voltage on the amount of sludge produced and consumption of energy (pH 7, 40 min, NaCl concentration of 0.5 g/L, Fe-anode, Al-cathode, initial diesel concentration of 3500 mg/L)



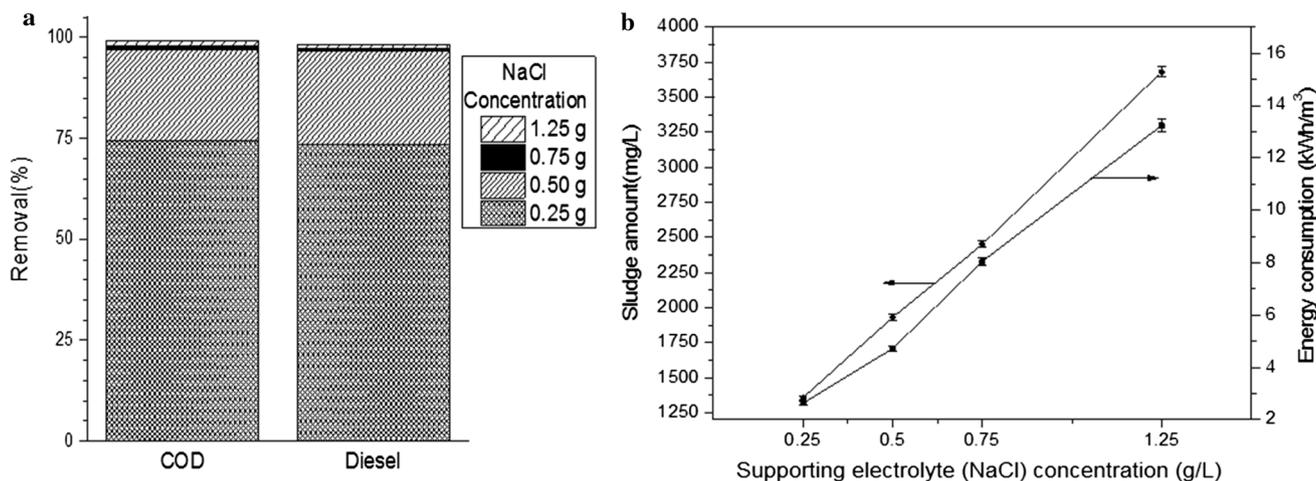


Fig. 5 **a** Effect of supporting electrolyte on the removal of COD and diesel and **b** effect supporting electrolyte concentration on the amount of sludge produced and consumption of energy (pH 7, 40 min, 10.5 V, Fe-anode, Al-cathode, initial diesel concentration of 3500 mg/L)

Effect of supporting electrolyte on electrocoagulation

In this section, different sodium chloride concentrations were used to evaluate the effect of the solution conductivity on EC. It should be noted that the solution conductivity affects the cell voltage, current efficiency and consumption of energy in electrolytic cell (Daneshvar et al. 2006).

The effect of supporting electrolyte on the removal efficiency of COD and diesel is shown in Fig. 5a. NaCl concentration was set in the range from 0.25 to 1.5 g/L. The removal efficiency of COD and diesel was 96.9 ± 1.2 and 96.8 ± 1.0 %, respectively, when NaCl concentration of the solution was 0.5 g/L. The removal efficiency was 99.1 ± 0.5 and 98.2 ± 0.4 % by adding 1.25 g/L of NaCl. Hence, the experiments were conducted at 0.5 g/L of NaCl due to negligible increase in removal. Moreover, almost no removal is observed without adding NaCl to the solution which is due to the fact that high electric conductivity is needed in order to use the EC's potential to remove the pollutants which synthetic oily wastewater does not possess it. This is in accordance with Yavuz et al. (2010) study.

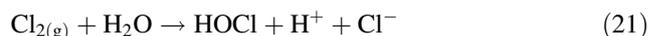
NaCl solution was selected as an electrolyte since it has several advantages, i.e., chloride ions could significantly reduce the adverse effects of other anions, such as HCO_3^- and SO_4^{2-} . The presence of the carbonate ion would lead to the precipitation of Ca^{2+} or Mg^{2+} ions that form an insulating layer on the surface of the electrodes. This insulating layer would sharply increase the ohmic resistance of the electrochemical cell and result in a significant reduction in the current efficiency and treatment conversion. Hence, it is suggested that among the present anions, there should be 20 % Cl^- to ensure a normal operation of EC in water treatment (Parsa et al. 2011).

Conductivity causes an increase in current density; thus, more amount of coagulant can be introduced to the media. In addition, NaCl causes an increase in Cl^- ions that chloride ions can remove the formed passivation layer on electrode surface (Chou et al. 2009). Thus, availability of metal hydroxide in the solution leads to an increase in the COD and diesel removal efficiency.

Molecular chlorine is produced during the electrolysis of chloride salts:



The produced molecular chlorine can then be hydrolyzed to hypochlorous acid and hypochlorite ions that these species are responsible for pollutants removal due to their high oxidative potentials (Janpoor et al. 2011).



This is consistent with findings of (Abdelwahab et al. 2009) when supporting electrolyte increases during the operation as the removal efficiency is increased.

The effect of supporting electrolyte concentration on the amount of sludge produced and consumption of energy is shown in Fig. 5b. By increasing the supporting electrolyte concentration from 0.25 to 1.25 g, the sludge formation rate from 1357 to 3680 mg/L and consumption of energy from 2.63 to 13.24 kWh/m³ are increased.

The results have shown that sludge production and consumption of energy were proportional to supporting electrolyte concentration. By increasing supporting electrolyte concentration, current and conductivity are increased during the process. Therefore, the amount of metal hydroxide formation, sludge production and consumption of energy are increased. In addition, the amount



of sludge produced increases by increasing the COD and diesel removal.

Effect of electrode material on electrocoagulation

Aluminum and iron are cheap, available and proved to be effective; hence, they were applied in the current study. The effect of electrode material on the removal efficiency of COD and diesel is shown in Fig. 6a.

As demonstrated in Fig. 6a, the pollutants removal efficiency was over 95 % for both electrode materials with an initial diesel concentration of 3500 mg/L. The results reveal that the aluminum electrode as anode and cathode has the highest effect on reduction in the COD and diesel from wastewater.

Iron electrode as sacrificial anode appeared greenish at first resulting from Fe^{2+} ions and then turned into yellow resulting from Fe^{3+} ion in the effluent. During the electrolysis of iron electrode, Fe^{2+} is the common ion produced. It can be oxidized easily into Fe^{3+} using dissolved oxygen in water. Moreover, there is Fe^{3+} in yellow particles of $\text{Fe}(\text{OH})_3$, and it is difficult to be settled. Furthermore, iron electrode becomes corroded at open circuit; therefore, the iron electrode is not preferred. Furthermore, effluent with aluminum electrodes was found very clear and stable (Chen et al. 2000; Kobya et al. 2006).

Conductivity of aluminum electrode is more than iron electrode, which results in greater formation of coagulant of aluminum into the media. Hydroxide of aluminum is more stable than hydroxide of iron and also absorption strength of hydroxide of aluminum is more than hydroxide of iron. Hence, the aluminum electrode for anode and cathode is chosen comparing to other electrode sets.

The effect of electrode material on the amount of sludge produced and consumption of energy is shown in Fig. 6b. The sludge formed and consumption of energy by aluminum electrode were more than the sludge formed and consumption of energy by iron electrode. As a result, the conductivity and coagulant formation by aluminum electrode are greater than iron electrode.

Effect of initial diesel concentration on electrocoagulation

The effect of initial diesel concentration was investigated from 3500 to 11,000 mg/L, and the removal efficiencies of COD and diesel are shown in Fig. 7a. The COD and diesel removal was decreased from 99.1 ± 0.2 to 49.1 ± 4.5 % and from 98.8 ± 0.2 to 45.5 ± 5.6 %, respectively, as the diesel concentration is increased from 3500 to 11,000 mg/L.

Removal efficiency for higher concentration of diesel is lower compared to its lower concentrations when using the conditions, which are optimized for lower concentrations. Since the formation amounts of the coagulant are insufficient, the EC process needs more time and voltage to achieve the same removal efficiency as concentrations is lowered. This is consistent with the study of (Canizares et al. 2007) for the COD removal efficiency from breakup of oil-in-water emulsions. They observed that the COD removal efficiency was decreased when oil concentration is increased.

The results in Fig. 7b have shown that sludge production and consumption of energy were proportional to the initial diesel concentration. By increasing the initial diesel concentration, current is increased during the process. Therefore, the amount of metal hydroxide formation, sludge production and consumption of energy are increased.

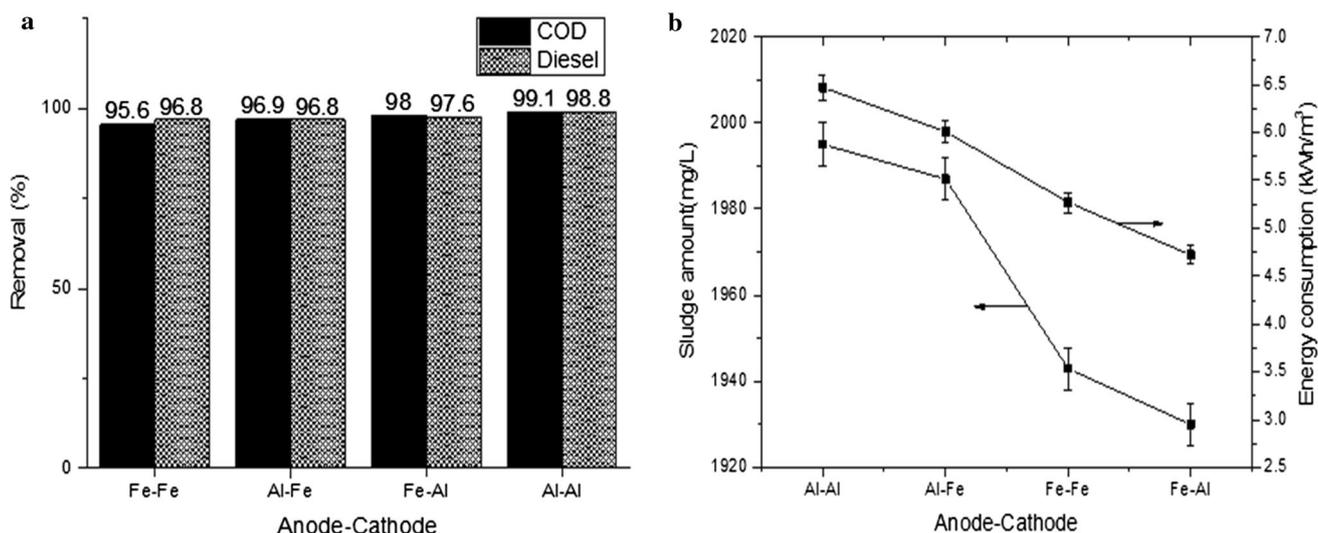


Fig. 6 a Effect of electrode material on the removal of COD and diesel and b effect electrode material on the amount of sludge produced and consumption of energy (pH 7, 40 min, 10.5 V, NaCl concentration of 0.5 g/L, initial diesel concentration of 3500 mg/L)

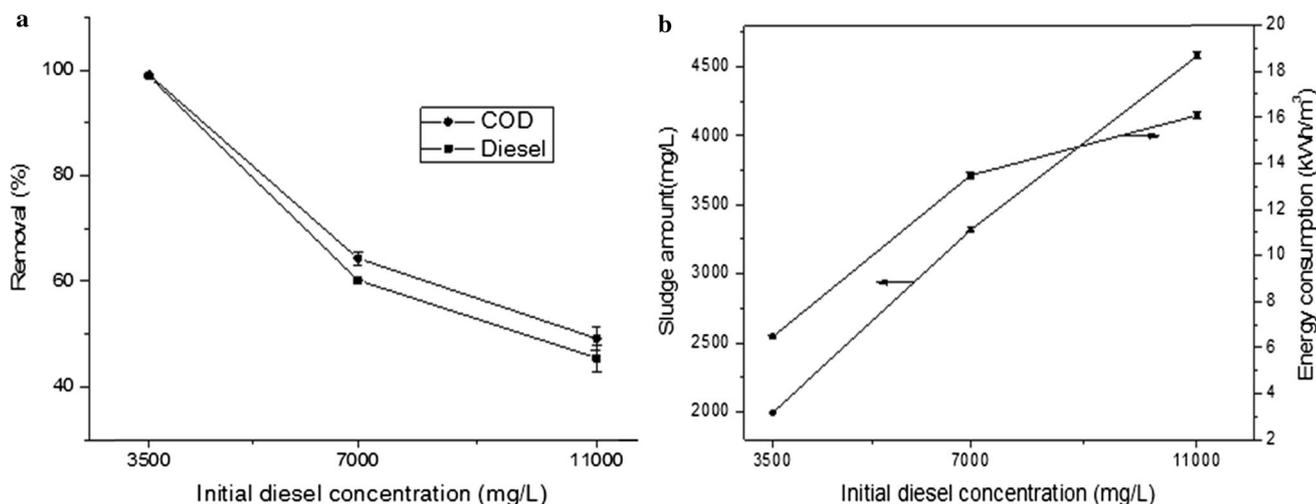


Fig. 7 a Effect of initial diesel concentration on the removal of COD and diesel and b effect of initial diesel concentration on the amount of sludge produced and consumption of energy (pH 7, 40 min, 10.5 V, NaCl concentration of 0.5 g/L, Al-anode, Al-cathode)

Summarily, the results have confirmed that sludge production and consumption of energy are proportional to voltage, time, the initial diesel concentration, as well as supporting electrolyte concentration; furthermore, there was a direct relationship between the amount of sludge formed and removal efficiency of the COD and diesel. In the optimal condition (pH 7, 10.5 V, 40 min, NaCl concentration of 0.5 g/L, Al-anode, Al-cathode and the initial diesel concentration of 3500 mg/L), the amount of sludge produced and the estimated consumption of energy were 1995 mg/L and 6.47 kWh/m³, respectively.

According to the Environmental Protection Agency (EPA), benchmark values for the COD and oil and Grease concentrations in stormwater are 120 and 15 mg/L, respectively. COD and diesel concentrations in the optimal condition (pH 7, 10.5 V, 40 min, NaCl concentration of 0.5 g/L, Al-anode, Al-cathode and initial diesel concentration of 3500 mg/L) were 15 and 42 mg/L, respectively. Thus, COD is below the limit recommended by EPA but further monitoring is required for oil and grease in order to ensure that the plant is successful in implementing Stormwater Pollution Prevention Plan (SWPPP) (EPA 2014). Even though the optimized EC process was not able to treat the diesel to its treatment limit, it was able to remove almost 99 % of influent concentration; therefore, it can be used as a pretreatment for this type of wastewater.

Determination of hydrocarbon types

In the optimal condition (pH 7, 10.5 V, 40 min, NaCl concentration of 0.5 g/L, Al-anode, Al-cathode and initial diesel concentration of 3500 mg/L), the samples were analyzed by the GC–MS to determine the types of hydrocarbons. The types of hydrocarbons and their removal efficiency are shown in Table 1.

Chromatogram of hydrocarbons before and after the treatment is illustrated in Fig. 8. As shown, nearly all hydrocarbons were removed.

Results' comparison with previous studies

1. One of the main advantages of EC is that short treatment time is required in comparison with other treatment methods. For instance, (Lohi et al. 2008) used three-phase fluidized bed reactor to achieve removal efficiency of 90 % for COD which took several days; however, in this research, EC method is used to achieve removal efficiency of 99 % for COD in 40 min.
2. The oil removal from oily wastewater by (Tir and Moulai-Mostefa 2008) has been achieved under this condition ($t < 20$ min, current density 25 mA/cm² and pH 7) and led to 90 % COD removal. (Ben Hariz et al. 2013) used this condition ($t = 30$ min, current density 21.2 mA/cm² and pH 9) to remove 80 % of the COD. However, in the present study, under this condition ($t = 40$ min, current density 3.125 mA/cm² and pH 7) 99 % of the COD is removed. Hence, the present study is able to achieve higher removal rate in more time and less current density.
3. Yavuz et al. (2010) have used EC to treat the refinery wastewater. Using iron electrode at current density of 1 mA/cm² and 120 min time, 2.26 % of the COD is removed; however, in the present study, by optimizing other parameters such as pH, voltage, electrode material and supporting electrolyte concentration over 2 log removal of COD has been achieved.
4. According to Asselin's results in Table 2 (Asselin et al. 2008), it can be concluded that by using aluminum electrode in the present study at the same current and less time, higher removal efficiency, less sludge production and consumption of energy have achieved.



Table 1 Identified compounds and their removal efficiency

Time (min)	Compound	Hydrocarbon group	Removal efficiency (%)
7.829	Nonane	Alkane	95
9.587	Benzene, 1-ethyl-3-methyl-	Aromatic	100
10.476	1,2,4-Trimethylbenzene	Aromatic	100
10.668	n-Decane	Alkane	100
11.228	Oxalic acid, 2-ethylhexyl nonyl ester	Polycyclic aromatic	100
13.165	Undecane	Alkane	97
15.886	Isododecane	Alkane	99
18.162	Naphthalene, 1-methyl-	Polycyclic aromatic	99
19.952	Dodecane, 2,6,11-trimethyl-	Branched alkanes	98
20.428	Tetradecane	Alkane	95
21.579	Nonadecane	Alkane	97
22.210	Pentadecane	Alkane	97
23.701	Cetane Hexadecane	Alkane	98
24.355	Octacosane	Alkane	100
24.621	Trimethylsilyl ether of glycerol	Ether	100
25.000	Heptadecane	Alkane	99
25.078	Hexadecane, 2,6,11,15-tetramethyl-	Branched alkanes	99
26.182	Heptadecane	Alkane	100
26.292	Hexadecane, 2,6,10,14-tetramethyl-	Alkane	100
27.268	Octacosane	Alkane	100
28.282	Pentadecane	Alkane	100
29.281	Furazan-3-carboxamide, oxime, 4-amino-N,N-dimethyl-	Aromatic	99

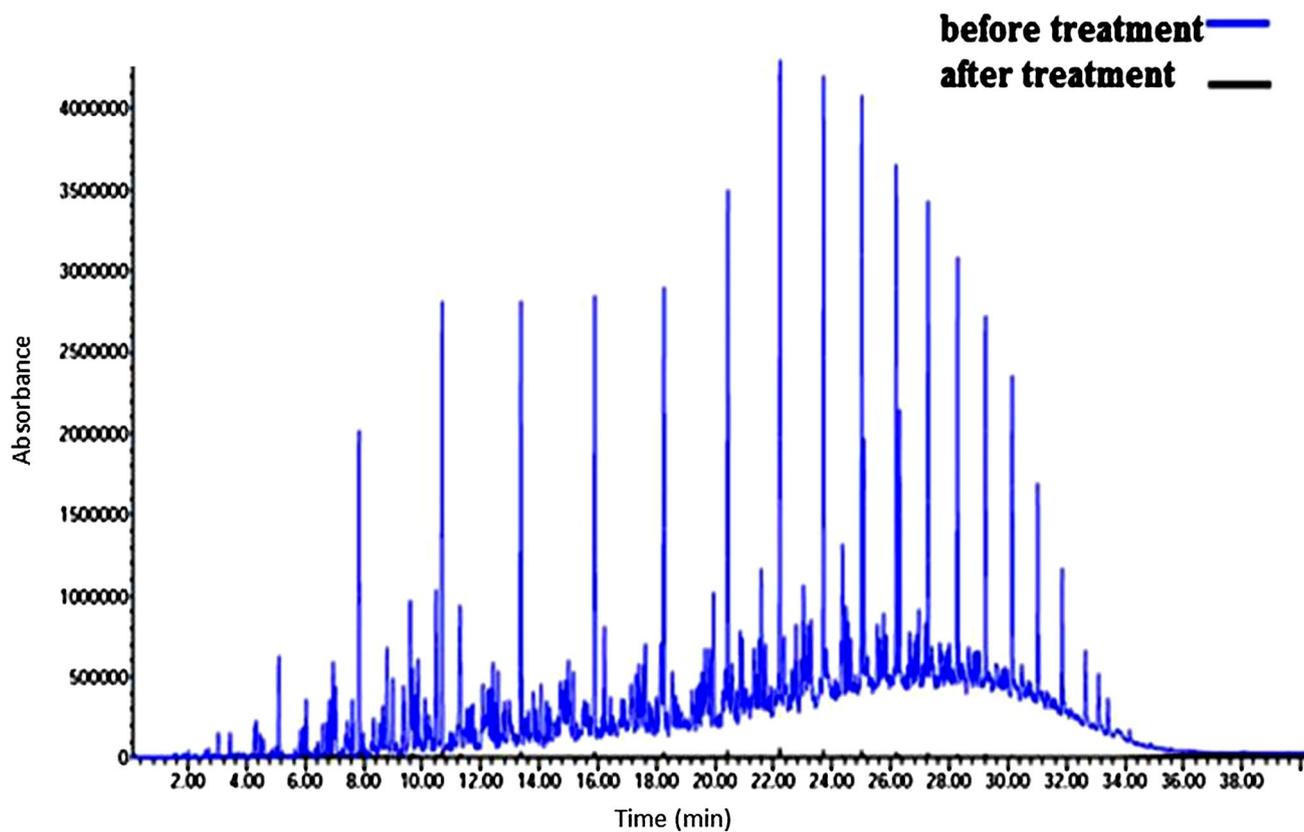
**Fig. 8** Chromatogram of hydrocarbon before and after treatment by electrocoagulation

Table 2 Asselin's results compared to the current study

Electrode material	Current (A)	Voltage (V)	<i>t</i> (min)	Consumption of energy (kWh/m ³)	Sludge production (kg/m ³)	COD removal (%)	References
Al	1.8	10.5	40	6.47	1995	99.1	In this article
Al	2	4.3	90	7.5	4940	74.7	(Asselin et al. 2008)
Fe	1.5	10.5	40	5.27	1943	95.6	In this article
Fe	1.5	3.1	90	4.04	2780	73.8	(Asselin et al. 2008)

5. El-Naas et al. have achieved 63 and 42 % removal for samples with initial COD concentrations of 596 and 4050 mg/L, respectively. Their results are achieved in 60 min time, pH 8, current density of 30 mA/cm², but in the present study, higher removal rate in less time and less current density have been achieved (El-Naas et al. 2009). Current results are in accordance with El-Naas results which removal efficiency is decreased by increasing the COD; however, in high COD the removal amount is higher. In addition, present results are compatible with (El-Naas et al. 2009) considering the use of aluminum as the most effective type of electrode.

Conclusion

In the current study, removal of COD and diesel from oily wastewater was investigated using electrocoagulation. The results of this study demonstrated that EC could be successfully used to remove the COD and diesel from synthetic wastewater contaminated by diesel. The effects of different parameters such as pH, time, voltage, supporting electrolyte, electrode material and diesel initial concentration on the treatment of this wastewater in a batch EC reactor were investigated.

According to this study, the pH has a considerable effect on the COD and diesel removal. The optimal initial pH for current experiments was 7. In addition, the pH of the wastewater was nearly constant during the process due to the buffering effect of the EC. The electrode arrangement of Al–Al as anode–cathode achieved the highest efficiency in reducing the COD and diesel. Increase in the voltage, time and NaCl concentration resulted in increase in removal efficiency, sludge production and consumption of energy. There was almost no removal for COD and diesel when no NaCl is added to the solution which is due to low conductivity of synthetic oily wastewater. Augmentation in the initial diesel concentration decreases the COD and diesel removal efficiencies but increases the sludge production and consumption of energy.

According to EPA, EC effluent of this study (15 mg/L COD and 42 mg/L diesel) is in compliance with discharge

regulations for COD, but further diesel removal is required in order to discharge current wastewater into aquatic medium. However, EC is a promising process for pre-treatment of oily wastewater. Furthermore, the buffering effect of the EC process allows the wastewater to be discharged without pH adjustments.

In summary, the highest removal efficiency for treating oily wastewater using EC was observed at pH 7, 40 min, 10.5 V, NaCl concentration of 0.5 g/L, aluminum as anode and cathode material, and initial diesel concentration of 3500 mg/L. In the optimized conditions, removal rates of 99.1 ± 0.2 % for the COD and 98.8 ± 0.2 % for the diesel are achieved. Moreover, the amount of sludge produced and energy consumption were 1995 mg/L and 6.47 kWh/m³, respectively.

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