# Removal of oil from biodiesel wastewater by electrocoagulation method

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**Abstract**−An attempt has been made to remove oil and grease (O&G) from biodiesel wastewater as well as O&G and turbidity in the presence of $H_2O_2$ and polyaluminum chloride (PAC), as a coagulant-aid by an electrochemical method using iron as sacrificial electrodes. The effects of current density, amount of hydrogen peroxide using as an oxidizing agent and addition of coagulant-aid, on percent removal and energy consumption have been investigated. The removal efficiency of O&G was in the range of 62-86%, whereas O&G removal was 100% in the current density range of 10-12.5 mAcm$^{-2}$ depending on the concentrations of $H_2O_2$ and coagulant aid. It is obtained that electrocoagulation in the absence of coagulant aid and oxidant is not too efficient for the treatment of this type of wastewater.

Key words: Electrocoagulation, Biodiesel Wastewater, Polyaluminum Chloride, Oxidant

## INTRODUCTION

Every year, a large volume of oily wastewater is produced by petrochemical, metallurgical, pharmaceutical, and food industries, resulting in terrible environmental pollution and resource utilization problems [1]. This wastewater must be treated before being released into the environment; otherwise, its high mineral and organic content may severely pollute coastal waters, estuaries, rivers, the seashore, soil, and even the air [2-5].

Conventional oily wastewater treatment methods, including gravity separation and skimming, air flotation, coagulation, de-emulsification and flocculation, have intrinsic disadvantages such as low efficiency, high operation cost, corrosion and recontamination problems [6]. More importantly, most of these conventional methods cannot efficiently remove the micron or submicron sized oil droplets [7,8].

Membrane technology is widely used to desalinate wastewater [9-11]. However, because of the presence of organic substances, such as dissolved oil in untreated oil field wastewater, the membrane equipment may become fouled, thus destabilizing the treatment process and increasing operation cost [12,13]. It is therefore desirable that any organic substances such as conventional activated sludge (CAS) process is commonly used to decompose organic substances in municipal wastewater because of its low cost and reasonable efficiency. However, as oil field wastewater is low in N and P compounds, the CAS process cannot operate efficiently over the long term, as bulking and foaming tend to occur [14,15]. Furthermore, the high salt concentration of oil field wastewater affects the metabolism of the microorganisms in activated sludge, causing plasmolysis and attenuating endogenous respiration [16].

Electrocoagulation has a long history as a wastewater treatment method, but it has never been accepted as a mainstream method [17]. In recent years, new processes for efficient and adequate treatment of various industrial wastewaters with relatively low operating costs have been needed due to strict environmental regulations. At this point, the electrocoagulation process has attracted a great deal of attention in treating industrial wastewaters because of its versatility and environmental compatibility. This method is characterized by simple equipment, easy operation, a shortened reactive retention period, a reduction or absence of equipment for adding chemicals, and decreased amount of precipitate or sludge which sediments rapidly. The process has been shown to be an effective and reliable technology that provides an environmentally compatible method for reducing a large variety of pollutants [18-20]. Moreover, during electrocoagulation, the salt content of the liquid salt content does not increase appreciably, as in the case of chemical treatment [19]. Nevertheless, electrocoagulation has been used to treat special wastewaters, such as oil wastes [21], black liquor from the paper industry [22], dye solutions and textile wastewaters [23] and nutrient enriched wastewaters [24]. Although electrocoagulation is primarily used to remove organic and suspended materials from various types of effluents, its use for iron removal from drinking wastewater [25], meanwhile this process is used for heavy metals removal from the pickling process of a billet plant [26] and COD, color and phenol from mill paper wastewater [27] has also been recorded. It was tested successfully to treat urban wastewater [28] and chemical fiber plant wastewater [29]. EC has also been proposed to treat various food industry wastewaters, such as yeast wastewater [30], olive oil wastewater [31,32], restaurant wastewater [33,34] and egg process wastewater [35].

In this study, removal of O&G from biodiesel wastewater was studied. Also the effects of different parameters such as current density, pH, temperature, operating time, coagulant and oxidant were investigated. Finally, the COD removal from biodiesel wastewater at optimum conditions was investigated.

## MATERIALS AND METHOD

### 1. Wastewater Characteristics

Wastewater was obtained from a tank containing a mixture of the biodiesel solutions at a biodiesel factory in Iran (Shahi). The

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**Table 1. Characteristics of wastewater**

| Parameter | Value |
|---|---|
| pH | 11.5 |
| COD (mgl$^{-1}$) | 22250 |
| Suspended matter (mgl$^{-1}$) | 613 |
| O&G (mgl$^{-1}$) | 6412 |
| Conductivity (µs cm$^{-1}$) | 360.4 |

composition of the wastewater is shown in Table 1. The O&G components in the wastewater were determined by a national standard method [36], using ultraviolet spectrophotometer (Analytik Jena AG Specord 200, Germany). COD, conductivity, pH, and TSS determinations were carried out as proposed by standard methods [37]. COD was measured using a COD reactor and direct reading spectrophotometer (DR/2000, HACH, USA). The pH and conductivity were adjusted to a desirable value by using NaOH or $H_2SO_4$, and NaCl, and measured by an AZ 8601 model pH meter, and a Lutron CD-4303 model conductivity meter, respectively.
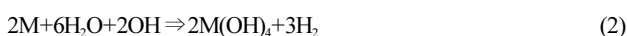
**2. Theory of EC**

EC processes (in batch mode) a direct current source between metal electrodes immersed in wastewater. The electrical current causes the dissolution of metal electrodes, commonly iron and aluminum into wastewater. The dissolved metal ions, at an appropriate pH, can form wide ranges of coagulated species and metal hydroxides that destabilize and aggregate the suspended particles or precipitate and adsorb dissolved contaminants. Generally, six main processes occur during EC: (i) migration to an oppositely charged electrode (electrophoresis) and aggregation due to charge neutralization; (ii) the cation or hydroxyl ion (OH$^-$) forms a precipitate with the pollutant; (iii) the metallic cation interacts with OH to form a hydroxide, which has high adsorption properties, thus bonding to the pollutant (bridge coagulation); (iv) the hydroxides form larger lattice-like structures and sweep through the water (sweep coagulation); (v) oxidation of pollutants to less toxic species; (vi) removal by electroflotation or sedimentation and adhesion to bubbles [38,39].

During the EC process, main electrochemical reactions at the cathode are: [40,41]

$H_2$ gas is liberated:

$$3H_2O + 3e \Rightarrow (3/2) H_2 + 3OH \tag{1}$$

The metal cathode (M) may be chemically attacked by OH especially at high pH values:

$$2M + 6H_2O + 2OH \Rightarrow 2M(OH)_4 + 3H_2 \tag{2}$$

At the anode, sacrificial metal (M), Fe, is dissolved:

$$M \Rightarrow M^{3+} + 3e \tag{3}$$

In the case of Fe electrode, the anodic reaction also occurs:

$$Fe \Rightarrow Fe^{2+} + 2e \tag{4}$$

In the case of Fe electrode; $Fe(OH)^{2+}$, $Fe(OH)_2^+$, $Fe_2(OH)_2^{4+}$, $Fe(OH)_4$, $Fe(H_2O)_2^+$, $Fe(H_2O)_5OH^{2+}$, $Fe(H_2O)_4(OH)_2^+$, $Fe(H_2O)_8(OH)_2^{4+}$, $Fe_2(H_2O)_6(OH)_4^{2+}$ are produced. Formation rates of these different species depend on pH of the medium and types of ions present, and play an important role in the EC process [42,43].



**Fig. 1. Experimental set up.**
1. Power supply      4. Wastewater
2. Electrolytic cell      5. Magnetic stirrer
3. Sacrifical electrodes

**Table 2. Characteristics of EC reactor**

| Electrodes | |
|---|---|
| Material (anode and cathode) | Iron (Fe) |
| Shape | Rectangular plate |
| Size (mm) | 65×72 |
| Number | 8 |
| Thickness (mm) | 3 |
| Plate arrangement | Parallel |
| Connection mode | Monopolar parallel |
| Effective electrode surface area (cm$^2$) | 80 |
| Reactor characteristics | |
| Make | acrylic material |
| Reactor mode | Batch |
| Dimensions (mm) | 240×110×110 |
| Volume (L) | 2.904 |
| Used wastewater volume (L) | 1.5 |
| Electrode gap (mm) | 10 |
| Power supply | |
| Voltage range (V) | 0-90 |
| Current range (A) | 0-18 |

**3. Electrolytic Cell**

The schematic diagram and characteristics of EC reactor are given in Fig. 1 and Table 2, respectively. The electrodes were installed on a perforated acrylic plate placed at 2 cm from the bottom of the cell. The eight electrodes were all individually connected to the dc power supply Xantrex XFR40-70 (Aca Tmetrix Inc., Ont., Canada); four anodes and four cathodes alternated in the electrode pack. The four electrodes connected to the positive outlet of power supply were consumed during the experiments, while the four cathodes were

insoluble (non-consumable electrodes). In a typical experiment, the specified volume of wastewater was poured into the cell, an initial sample was taken and the current was then applied under regular magnetic stirring. Different samples of 5 ml were taken at 10 min intervals for up to 1 h and filtered before being analyzed to determine the O&G. A gentle stirring rate of about 200 rpm was applied to allow the chemical precipitate to grow large enough for removal [44]. The pH was adjusted to a desired value using HCl and NaOH solutions. The electrodes were placed into the reactor. The reaction was timed, starting when the DC power supply was switched on. One of the greatest operational issues with EC is electrode passivation. During EC process, an oxide layer was formed at the anode. Eliminating the oxide formation at the anode could reduce this effect, so before each run electrodes were washed with acetone to remove surface grease, and the impurities on the iron electrode surfaces were removed by dipping for 5 min in a solution freshly prepared by mixing 100 cm³ HCl solution (35%) and 200 cm³ of hexamethylenetetramine aqueous solution (2.80%) [45]. All the experiments were repeated twice, and the experimental error was below 4%; the average data were reported. The efficiency of O&G % Removal was calculated as

$$\% \text{ Removal} = \frac{C_i - C_f}{C_i} \times 100 \tag{5}$$

Where $C_i$ is the initial materials concentration (mg L⁻¹) and $C_f$ is the final materials concentration (mg L⁻¹).

## 4. Biodiesel Production Process

Generally, all biodiesel production factories have almost the same processes. They begin with the mixing process of alcohol and catalyst for homogenization. Then the mixed solution is fed to react with oil or fat in the reactor where the transesterification reaction occurs in this section. The reaction mix is kept just above the boiling point of the alcohol to speed up the reaction and the reaction takes place. The products mixture, methyl ester and glycerin, undergo a separation process before excess alcohol from each fraction is removed by distillation and is reused. The methyl ester is purified by washing with warm water to remove residual catalyst or soaps and dried prior to storage, while glycerin is sometimes neutralized with an acid and sent to storage as crude glycerin. However, each factory that has different raw material has different oil or fat preparation step.

## RESULTS AND DISCUSSION

### 1. Effect of Operating Time and Current Density on the Removal Efficiency

Operating time experiments were performed at pH 7. Batch electrocoagulation experiments were conducted for 25 min for different current densities. Fig. 2 shows the effect of current density, c.d, on electrocoagulation. As can be seen, O&G removal increases with increasing time. After 25 min the O&G concentration was reduced to 3,211 ppm, 2,200 ppm, 1,500 ppm and 1,100 ppm for current densities of 2.5, 5, 7.5 and 10 mA cm⁻², respectively. The higher (>10 mA cm⁻²) current density has not significant effect on the removal efficiency of O&G. This is ascribed to the fact that at high current densities the dissolution of anode electrode increases according to Faraday's law; the resulting metal hydroxides produces more sludge with a consequent significant removal of phenol due to sweep
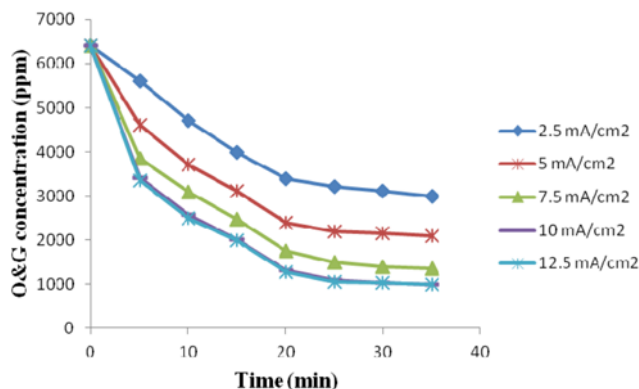
Fig. 2. Effect of electrolysis time and current density on O&G removal (pH: 7, and temp: 20 ℃).

coagulation [46]. An oil-water emulsion is a colloidal dispersion in which oil constitutes the dispersed phase and water forms the continuous phase. Emulsions are normally stabilized by the presence of an emulsifying agent, such as a surfactant. The anionic head groups on the surfactant molecules prevent aggregation and coagulation of the oil droplets via electrostatic repulsion. During electrolysis in an EC procedure, the sacrificial iron anode is oxidized to polymeric ionic species. With progressive electrolysis, the ionic strength of the medium increases. Ionic polymeric iron species can neutralize the surface charge of surfactant molecules. They can generate bridges between surfactant molecules. Simultaneously, hydrogen as well as hydroxides is generated at the cathode. The pH of the medium rises as a result of this electrochemical process. The net result of the reactions is that the emulsion is destabilized, and the colloidal

Table 3. Consumption of Iron, removed O&G (g) from wastewater and Fe consumption (g) Iron/g O&G

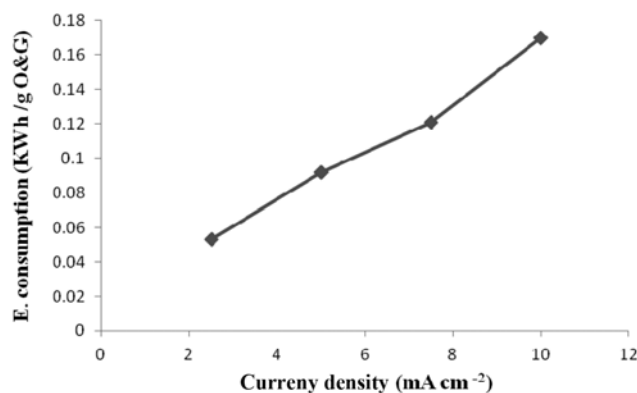| Current density (mAcm⁻²) | Fe consumption based on Faraday's law (g Fe) | removed O&G (g) from wastewater | Fe consumption (g) Iron/g O&G |
|---|---|---|---|
| 2.5 | 5.05 | 8.01 | 0.63 |
| 5 | 10.1 | 10.5 | 0.96 |
| 7.5 | 15.15 | 12.3 | 1.23 |
| 10 | 20.2 | 13.28 | 1.51 |



Fig. 3. Effect of current density on energy consumption (pH: 7, temp: 20 ℃, and time: 25 min).

oil particles begin to coalesce [47].

For the same operating conditions, after 25 min of electrocoagulation, consumption of energy and electrode material is also represented in Table 3 and Fig. 3. Energy consumption is expressed as:

$$E.Consumption = \frac{IVt}{m} \qquad (6)$$

where E.Consumption, I, V, t and m are energy consumption (kW h g$^{-1}$ of O&G removed), applied current (A), voltage (V), retention time (s) and the weight of the O&G removed from wastewater (g), respectively. The iron electrode consumption having a unit of g Fe g$^{-1}$ of O&G removed is calculated from Faraday's law from the following relation:

$$Fe\ Consumption = \frac{ItM}{zF} \qquad (7)$$

where F is the Faraday's constant (96,500 C mol$^{-1}$), M the molecular weight of iron (26 gmol$^{-1}$) and z is the number of electron transfer ($z_{Fe}$=2), respectively. Fe consumption and E. consumption were found to increase with increasing the current density (Table 3 and Fig. 3). An increase in current density from 2.5 to 10 mA/cm$^2$ causes an increase in energy consumption from 0.053 to 0.17 kW h g$^{-1}$ and electrode consumption from 0.63 to 1.51 g Fe g$^{-1}$ of O&G.

Table 3 has 3 columns that in these columns Fe consumption (based on Faraday's law), amount of O&G removed from wastewater, and amount of g Fe g$^{-1}$ of O&G are calculated. The data shows both of amounts of Fe and removed O&G increase by increase of current density. Meanwhile the amount of g Fe/g of removed O&G increase. Also the concentration of iron in the wastewater is measured by atomic absorption. It was found that the concentration of iron in the wastewater increased.

## 2. Influence of Initial pH

It is known that initial pH and applied voltage (or current density) can influence the coagulant dosage rate and bubble generation rate, which in turn affects the pollutant removal efficiencies [48]. To determine the effect of initial pH on the concentration of O&G, the pH of biodiesel wastewater was adjusted with either HCl or NaOH. In each batch experiment, the current density and reaction time were kept constant at 10 mA/cm$^2$ for 25 min. As shown in Fig. 4, the O&G concentration decreased as the initial pH decreased to the acidic level. At pH 7, the lowest concentration is achieved. For removal
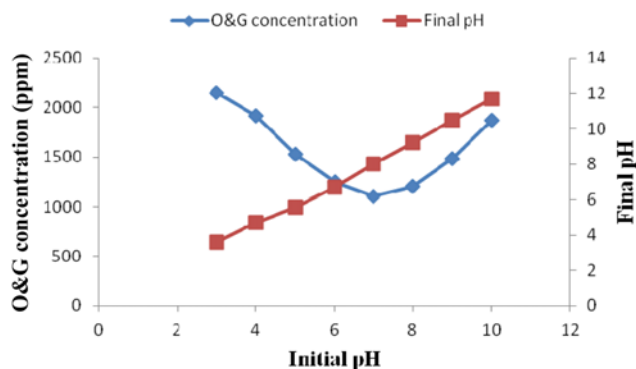


Fig. 4. The effect of pH on the O&G removal (c.d: 10 mA/cm$^2$, temp: 20 °C and operation time: 25 min).
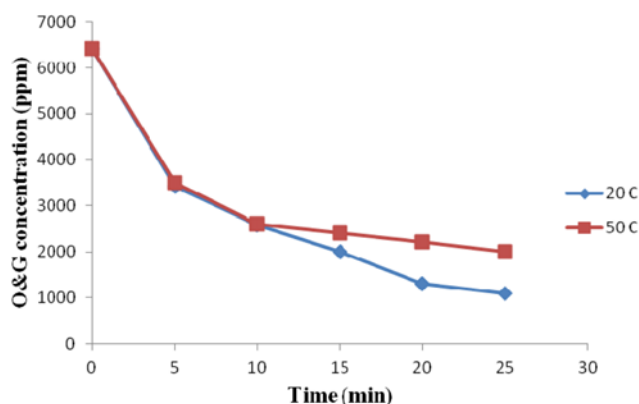


Fig. 5. Effect of temperature on the removal of O&G (c.d: 10 mA/cm$^2$, pH: 7).

mechanisms of O&G, it was found that colloidal particles in the pH range 6-7 contribute to the formation of amorphous hydroxide precipitates and other iron hydroxo complexes with hydroxide ions and polymeric species. As pH increased to 8, an increase of O&G concentration is observed due to the less formation of the reactive ocs of iron hydroxide. In the basic range, iron hydroxide ions may form negatively-charged ions such as Fe(OH)$_4$ which allow less eective occulation. Since hydroxide ions are produced along with H$_2$ bubbles at the cathode (Reaction (1)), it contributes to increase the final pH of the treated wastewater.

## 3. Effect of Temperature

Temperature is always considered an important parameter in any chemical or electrochemical separation process. The effect of temperature on the removal of O&G from aqueous solution was evaluated at two different temperatures, 20 °C and 50 °C, and a constant current density of 10 mA/cm$^2$, where the temperature was controlled by using a water bath (Schutzart DIN 4050-IP 20, Germany). The results are presented in Fig. 5 for the O&G concentration. For the first 10 min of electrolysis, the temperature has negligible effect on the component removal. However, after 10 min, the O&G concentration at 50 °C becomes slightly higher than that at 20 °C. The increase in the temperature of the solution results in increasing the solubility of iron. Therefore, the precipitation of the iron is enhanced at lower temperatures, which results in a better removal.

## 4. Effect of Coagulant and Oxidant Effect

Coagulants change surface charge properties of solids to promote agglomeration and/or enmeshment of smaller particles into larger flocs. These larger agglomerates are removed by sedimentation and/or filtration. The polyaluminum chloride as a coagulant-aid was used in the experiments to increase the removal efficiency. Fig. 6 shows the concentration of O&G in EC process in presence of coagulant. The results show that the removal of O&G from the aqueous solution was effected with polyaluminum chloride (PAC) dosage in the range of investigation and increase the amount of PAC reduce the O&G concentration in the wastewater. On other hand, the higher amount of PAC (>0.5 g L$^{-1}$) has not significant effect on the O&G removal (the concentration of O&G reduced from 6412 to 387 when the concentration of PAC was 0.5 g L$^{-1}$). When the electrocoagulation was conducted with coagulant-aid, a higher removal of O&G was achieved. Moreover, it was observed that ocs
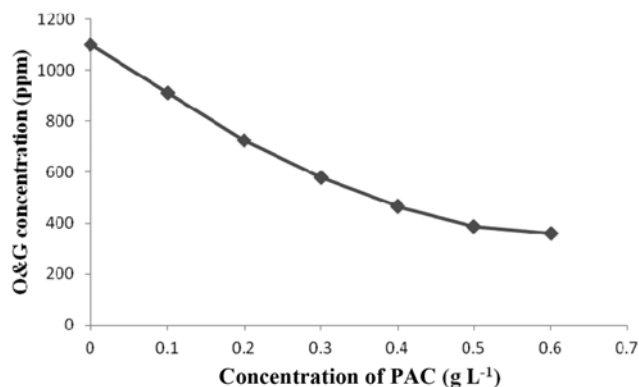
**Fig. 6. The variation of final O&G concentrations for different a-mount of PAC (c.d=10 mAcm⁻², pH: 7, operation time: 25 min, Temperature: 20 °C).**



**Fig. 8. The effect of $H_2O_2$ concentration on the conductivity of waste-water.**

formed in that process exhibited a greater surface, enlarging their settle ability.

In the last decade, a special type of electrochemical reaction, the electro-Fenton system, has attracted considerable research interest. These are of three main types: in the first (EF-$H_2O_2$ method), $H_2O_2$ is electrogenerated from two-electron reduction of sparged oxygen on the cathode while $Fe^{2+}$ is added; the second (EF-Feox method) uses added $H_2O_2$ and electrogenerated $Fe^{2+}$ which is produced via the oxidation of iron, the sacrificial anode; and in the third type, $H_2O_2$ is added while $Fe^{2+}$ is electrogenerated via the reduction of ferric sulfate or ferric hydroxide sludge [49,50]. In this study, the electrolysis of the biodiesel wastewater using iron electrodes was conducted using the second type of electro-Fenton system. In such a system, the main oxidizing agents are the hydroxyl radicals (˙OH) that are generated via the reduction of $H_2O_2$ with ferrous ion (Eq. (8)) produced at the anode [49].

$$H_2O_2 + Fe^{2+} \rightarrow H^+ + OH^- + Fe^{3+} \qquad (8)$$

Due to the strong oxidizing potential of the hydroxyl radicals, the organic pollutants were readily oxidized. This feature was evaluated in the experiments to increase O&G removal by adding hydrogen peroxide. O&G concentration is shown in Fig. 7 in the EC process for different $H_2O_2$ concentrations. As can be seen, the concentra-
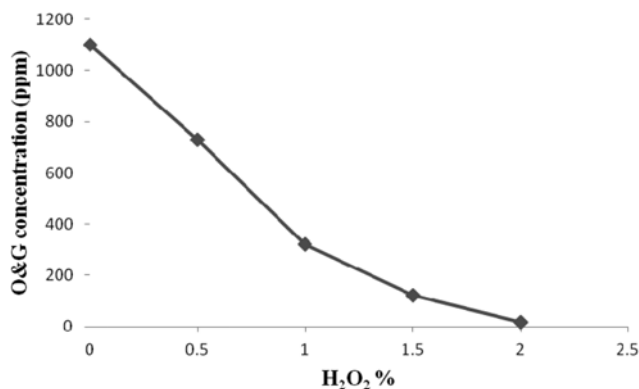
tion of O&G was reduced from 6,412 ppm to 18 ppm, when the concentration of $H_2O_2$ was 2%. Electrical conductivity of the solution is relatively high; the gas sparging operation, plus the generation of hydrogen gas in situ, produces a relatively large gas fraction which significantly reduces the effective electrolyte conductivity. The results indicate that the electrocoagulation in the presence of coagulant-aid and oxidant was more effective for the treatment of this type of wastewater. Meanwhile, the relation between $H_2O_2$ concentration and conductivity is shown in Fig. 8. As can be seen, the conductivity of wastewater increased by increase the $H_2O_2$ concentration.

Fig. 9 shows the O&G concentration after electrocoagulation process at different current densities (2.5, 5, 7.5, 10 mAcm⁻²) in presence 2% $H_2O_2$ and 0.5 g L⁻¹ PAC. The pH and temperature of solution are 7 and 20 °C, respectively. O&G concentration is lower than Fig. 2. In the presence of $H_2O_2$ and PAC, the required time for electrocoagulation process and final O&G concentration are decreased. Meanwhile in 10 mAcm⁻², the total O&G in the wastewater is removed, so that these results show the electrocoagulation process with the aid of PAC and $H_2O_2$ can be very effective in the O&G removal from wastewater.

When PAC is dissolved in water, the metal ions hydrate and hydrolyze to form monomeric and polymeric species: $M(OH)^+$, $MOH^{2+}$, $M_2(OH)_2^{4+}$, $M(OH)_4^{5+}$, $M(OH)_2$ (s) and $M(OH)_4^-$ etc. At low pH (pH<



**Fig. 7. The variation of final O&G concentrations for different per-cent of $H_2O_2$ (c.d=10 mAcm⁻², pH: 7, operation time: 25 min, Temperature: 20 °C).**
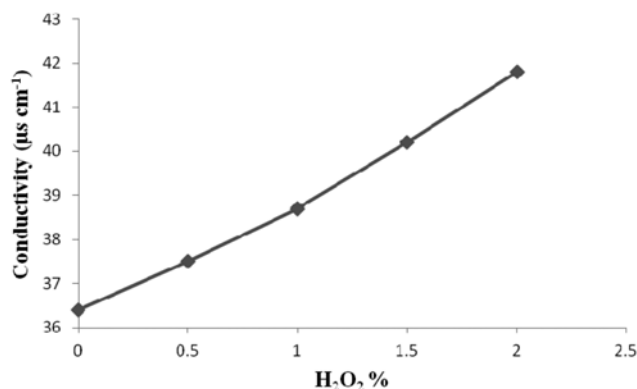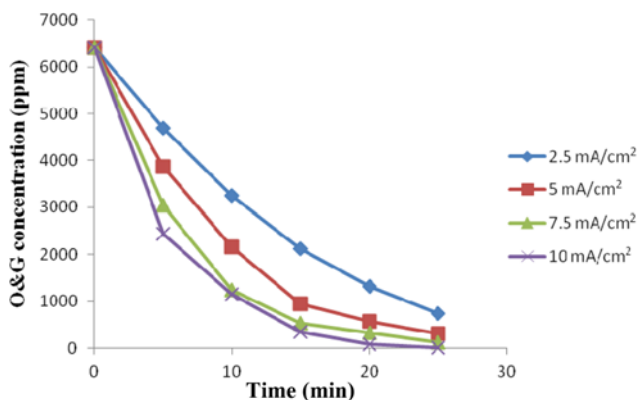


**Fig. 9. Effect of electrocoagulation time and current density on O&G removal in presence of 2% $H_2O_2$ and 0.5 g L⁻¹ PAC (pH: 7, and temp: 20 °C).**

7), $Al^{3+}$ remain in the solution and form precipitates of $Al(OH)_3$ as the pH is increased or as the coagulant dosage is raised [51]. The general form of hydrolysis reaction of trivalent metals is represented as [52]:

$$x\ M^{3+}+y\ H_2O=Mx(OH)y^{(3x-y)+}+y\ H^+ \tag{9}$$

The metal hydroxide polymers have amorphous structure, very large surface area, and possess positive charge [53]. These hydroxides are hydrophobic, causing them to adsorb onto the organic anionic particle surface and become insoluble [51,52]. Aluminum cations tend to associate and complex with a number of functional groups and ligands, especially with polar molecules and with oxygen containing functional groups like hydroxyl and carboxylic groups [53-55]. The local negative charge of these groups is neutralized by the Al cations, resulting in colloid destabilization and precipitation of the metal (cations) organics (anions) complexes. This phenomenon induces sweep flocculation and the adsorption and bridging enhancement of both particulate organics and inorganic solids to form large, amorphous flocs [56]. The precipitation is enhanced as the pH is lowered in the presence of multivalent cations.

During the Electro-Fenton process, the molecular oxygen and ferric ions are simultaneously reduced at the cathode to generate hydrogen peroxide and ferrous ions according to reactions (10) and (11):

$$O_2+2e^-+2H^+ \rightarrow H_2O_2 \tag{10}$$

$$Fe^{3+}+e^- \rightarrow Fe^{2+} \tag{11}$$

The classical Fenton's reaction (8) then takes place in solution to generate · OH radicals. The ferrous ions produced by reaction (8) are regenerated by reaction (11). The Fenton's reagent ($H_2O_2$, $Fe^{2+}$) used in this reaction is generated in situ and in a catalytic way by electrochemistry [57,58]. Hydroxyl radicals then react on organic compounds by three types of reactions: hydrogen atom abstraction, electrophilic addition on double bond, and electron transfer:

$$RH+OH^{\cdot} \rightarrow H_2O+R^{\cdot} \tag{12}$$

$$PhX+OH^{\cdot} \rightarrow PhXOH^{\cdot} \tag{13}$$

$$RX+OH^{\cdot} \rightarrow RX^{\cdot+}+OH^{\cdot} \tag{14}$$

In all cases, the first reaction intermediate is a radical species. Further reactions, which occur with the participation of hydroxyl radicals, molecular oxygen, ferrous and/or ferric ions, lead finally to the mineral end products [57]. The Electro-Fenton process presents the following major advantages: no addition of chemical reagent except a catalytic quantity of ferrous ions, no pollution displacement to another medium and complete degradation of toxic organic pollutants. Fenton's reagent constitutes an efficient oxidant for a great variety of organic substrates. The electrochemistry offers the opportunity to produce this reagent in situ in aqueous medium. It is sufficient to apply a low cathodic potential to the working iron electrode to start

the production of Fenton's reagent and, consequently, the hydroxyl radicals. At this potential, two cathodic reactions take place simultaneously: reduction of dioxygen to hydrogen peroxide (reaction 10) and reduction of ferric ions to ferrous ions (reaction 11). Oturan and Pinson suggest the formation of $H_2O_2$ in several steps: first, dissolved dioxygen is reduced to superoxide ion, $O_2^-\cdot$ (reaction 15) which reacts quickly with $H^+$ in acidic medium to produce peroxyl radical $HO_2\bullet$ (reaction 16):

$$O_2+e^- \rightarrow O_2^{-\cdot} \tag{15}$$

$$O_2^-\cdot+H^+ \rightarrow HO_2\bullet \tag{16}$$

This radical is unstable and finally leads to the formation of hydrogen peroxide:

$$HO_2\bullet \rightarrow H_2O_2+O_2 \tag{17}$$

However, this approach requires a permanent supply of dioxygen. To resolve this issue, the electrolysis can be realized in an undivided cell where dioxygen is produced in situ by oxidation of water at the Pt anode. Thus, the transport of the hazardous oxidant ($H_2O_2$) becomes unnecessary, and the quantity of oxidant can be precisely controlled [57,58]. The production of hydroxyl radicals via electrochemically assisted Fenton's reaction constitutes a catalytic system. The hydroxyl radical production takes place in homogeneous solution, where they react on the organic compounds present in the medium. Reactions are particularly complex and depend on experimental conditions. They take place in several steps with hydroxyl radicals, molecular oxygen, and ferrous and/or ferric ions taking part and lead finally to the mineralization of the initial organic compound [59].

## 5. Study the COD Removal from Wastewater in O&G Removal Optimum Conditions

The concentration of COD after electrocoagulation process is indicated in Table 4. The current density, electrocoagulation time and pH were 10 $mAcm^{-2}$, 25 min, 7, respectively. As can be seen, this process is effective for treatment of COD from wastewater. Also, the $H_2O_2$ and PAC have considerable effect in the COD removal. Meanwhile, the application of both of $H_2O_2$ and PAC has effectiveness and COD removal is increased.

## CONCLUSION

This investigation has demonstrated that electrocoagulation with iron electrodes is an effective method to clarify biodiesel wastewater by reducing the O&G content of the wastewaters. Electrocoagulation is a feasible process for treating the biodiesel wastewater, characterized by high O&G concentrations. The effect of various operational parameters on electrocoagulation operation was investigated and optimized. The results showed that O&G was effectively removed at initial pH 7 when the initial concentration of O&G was 6,413 mg $L^{-1}$. The optimal current density for O&G removal

**Table 4. COD concentration after electrocoagulation process in optimum conditions**

|  | Electrocoagulation process without PAC & $H_2O_2$ | Electrocoagulation process by 0.5 g PAC | Electrocoagulation process by 2% $H_2O_2$ | Electrocoagulation process by 0.5 g PAC & 2% $H_2O_2$ |
|---|---|---|---|---|
| O&G concentration (ppm) | 11781 | 6741 | 4238 | 1323 |

was 10 mA/cm$^2$ for an operating time of 25 min. At above optimal conditions, the final concentration and power requirements were 1,098 ppm and 0.43 kWh/g O&G. The effect of temperature on the electrocoagulation process was investigated in two temperatures (20 °C and 50 °C), and it was found that the electrocoagulation process was most effective at low temperature (20 °C). Differences between treatment efficiencies with and without H$_2$O$_2$ and PAC were found to be significant. The best results have been achieved in electrocoagulation enhanced with coagulation and oxidation using 2% H$_2$O$_2$+0.5 g L$^{-1}$ PAC. The final concentration of O&G in electrocoagulation by 2% H$_2$O$_2$ and 0.5 g L$^{-1}$ PAC was 18 ppm, 387 ppm. Also, total O&G is removed when electrocoagulation process by 2% H$_2$O$_2$+0.5 g L$^{-1}$ PAC is used. The relation between conductivity and percentage of H$_2$O$_2$ was investigated, that results show increase the amount of H$_2$O$_2$ increase conductivity. Meanwhile, the COD removal was investigated in optimum conditions that it was found this process enhanced with H$_2$O$_2$ & PAC is effective for the COD removal from biodiesel wastewater. The concentration of COD after treatment by electrocoagulation process and 2% H$_2$O$_2$+0.5 g L$^{-1}$ PAC reduce from 22,250 ppm to 1,323 ppm.

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