Treatment of Al-Muthanna Petroleum Refinery Wastewater by Electrocoagulation Using a Tubular batch Electrochemical Reactor

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Abstract. An electrocoagulation process has been used to eliminate the chemical oxygen demand (COD) from wastewaters discharged from the Al-Muthanna petroleum refinery plant. In this process, a circular aluminum bar was used as a sacrificial anode, and hallow cylinder made from stainless steel was used as a cathode in a tubular batch electrochemical Reactor. Impacts of the operating factors like current density (5-25mAcm⁻²), NaCl addition at concentrations (0-2g/l), and pH at values (3-11) on the COD removal efficiency were studied. Results revealed that the increase in current density increases the COD removal efficiency, whereas an increase in NaCl concentration results in a decline in the COD removal efficiency. Using a pH value higher or lower than 7 causes a lowering of the COD removal efficiency. A current density of 15mA/cm², NaCl concentration of 1g/l, and pH value of 7 were found to be the best operating conditions in which COD removal efficiency of 95.3% was achieved at a treatment time 45 minutes with an energy consumption of 27.78kWh/kg COD. Based on these conditions, a COD value of 20 ppm could be obtained, which is below the standard limit for discharging petroleum refinery effluents.

Keywords: COD removal, Electrocoagulation, Petroleum refinery wastewater, aluminum anode.

1. Introduction
Treatment of the effluents discharged from various sectors of industries is considered an important challenge due to the enormous amounts and the different types of pollutants existing in these effluents. The petroleum refinery process is one of these industries that generates huge quantities of water during different stages like thermal cracking, hydrotreating, distillation, desalting, and cooling systems [1]. It was reported that the quantity of wastewater in term of volume unit that generated from petroleum refining processes is 1.6 times the quantity of the crude oil that has been processed. Besides, nearly 80-90% of the water utilized in the petroleum refinery process is discharged as wastewaters. Hence, treating these effluents has the benefit of reusing the water again in addition to solving environmental pollution issues [2]. Characteristics of petroleum refinery discharge always vary according to the types of oil, the configuration of the plant, and the mode of production [3]. Nevertheless, effluents from refinery processes contain aliphatic and aromatic compounds at a high level of concentration leading to damaging and destructive effects on the environment [4]. The traditional treatment of the wastewater originated from the refineries is based on mechanical and physicochemical methods such as oil–water separation and coagulation followed by biological Treatment [5]. However, these methods produced huge quantities of sludge and suffered from several technical and economic
disadvantages. Hence, a feasible and effective method should be adopted to treat the effluents discharged from petroleum refinery processes.

Various approaches have been utilized to treat the effluents discharged from a petroleum refinery, such as Fenton and photofenton processes [6], enhanced photo-degradation [7], membrane bioreactor [8], flocculation and ceramic membrane filtration [9], and electrochemical processes [4]. Electrochemical systems like Electrocoagulation (EC) and electrooxidation (EO) have many advantages, such as easiness of distribution and a minimum amount of chemicals that can be used. In the last few years, numerous papers have addressed that the Electrocoagulation is an efficient method that can be used for treating wastewaters having finely dispersed particles [10]. This method is a compact and robust system that replaced the processes of the traditional method, which required a vast quantity of chemicals [11]. In this method, a sacrificial anode was utilized to generate various monomeric and polymeric composites of metal ions via its dissolution due to the applying of an electrical current. These ions destabilize the colloidal contaminants in the wastewater and forming flocs that adsorb the dissolved composites [12, 13]—for example, applying an electrical current across a cell composed of stainless steel cathode and Al anode results in generating aluminum ions from the surface of the anode which reacts with OH⁻ ions that generated on the cathode due to water reduction leading to the creation flocs of amorphous Al(OH)₃(s) (Eqs. (1)–(4)). Simultaneously, oxygen and hydrogen gases are released at the anode and cathode, respectively (Eqs. (2) and (3)). These gases permit accumulating the flocs via flotation at the surface of liquid [14] while heavier stay at the cell bottom by means of sedimentation. The reactions that occur in the electrocoagulation process can be summarized as follows:

At the anode:

\[(Al)_s \rightarrow Al^{3+} + 3e^- \]  
\[2H_2O \rightarrow O_2(g) + 5H^+ + 5e^- \]  

At the cathode:

\[2H_2O + 2e^- \rightarrow H_2 + 2OH^- \]  

In solution

\[Al^{3+} + 3OH^- \rightarrow Al(OH)_3(s) \]  

Numerous types of wastewaters have been treated by Electrocoagulation, such as petroleum hydrocarbons removal from oil refinery effluent [15]; textile industry effluents [16]; heavy metals such as Zinc and copper from oil refinery wastewater [17]; removal of chromium from tannery effluents [18]; removing of color from molasses of sugar beet [19], and removing of phosphate from mining effluents [20].

In the present work, an electrocoagulation process based on a tubular electrochemical reactor design has been applied to remove COD from Al-Muthanna petroleum refinery wastewater where the impacts of operational factors like current density, NaCl addition, and pH on the efficiency of COD removal have been investigated.

2. Materials and methods

Thirty liters of Al-Muthanna petroleum refinery wastewater have been collected from the plant discharge point and stored at a temperature of 4 ºC until use. Table 1 shows the characteristics of Al-Muthanna petroleum refinery wastewater. The quantity of wastewater generated daily from this plant was approximately 25m³/d based on the statistical data provided by the administration of the plant.

| Parameters        | Value |
|-------------------|-------|
| COD (mg/l)        | 425   |
| pH                | 8     |
| T.D.S (mg/l)      | 1325  |
| Cl⁻ (mg/l)        | 456   |
| SO₄²⁻(mg/l)       | 34    |
| Turbidity NTU     | 3.35  |
| Conductivity (µS/cm) | 5350 |
A tubular electrochemical cell fabricated from Perspex glass with dimensions (100 mm inside diameter, 140 mm length) was used. It was provided with a Perspex cover with dimensions (150 mm outside diameter, 10 mm thickness) having a hole for fixing of the anode and two holes to put the probes of conductivity and pH-meters.

A configuration based on concentric electrodes arrangement was implemented for the electrocoagulation process where cylindrical stainless steel has dimensions (90mm inside diameter x 100mm length x 3mm (thickness)) was used as cathode and Aluminum bar (50mm in diameter x 125mm length) with an active surface area of 157cm$^2$ was used as the anode. The space between the anode and cathode was hold at 20 mm. The constant current operation was adopted using a digital power supply, Type UNI-T (UTP1305, Hong Kong). A 0.5 L solution of wastewater was firstly agitated at the rotation speed of 150 rpm using a magnetic stirrer, then regulated its pH using (1M) NaOH or (1M) HCl for the suitable run condition, and finally put inside the cell. All runs were conducted at room temperature (25 ºC). Fig.1 shows the schematic diagram of the electrocoagulation system. A digital pH meter (HNNA Instrument Inc, PH211, Romania) was used to detect the pH of the solution, while HM digital meter, model COM-100, Korea, was used to measure the conductivity and TDS of the solution. At every 10 minutes of electrolysis, samples were taken and analyzed for COD value using thermos-reactor (RD-125, Lovibond) in combination with spectro-photometer (MD-200, Lovibond). Measurement of COD were performed triple for each sample and the mean value was taking in this work.

![Fig. 1. The electrochemical apparatus](image)

COD removal efficiency (RE%) was estimated by Eq. (5), [21]:

$$RE\% = \frac{C_i - C_f}{C_i} \times 100$$  \hspace{1cm} (5)

where $C_i$ is the initial concentration (mg L$^{-1}$) and $C_f$ is the final concentration (mg L$^{-1}$).

The energy consumption (EC) was calculated using Eq.6 in term of (kWh/kg COD) [22]:

$$EC = \frac{U \cdot I \cdot t \times 1000}{(COD_i - COD_f) \cdot V}$$ \hspace{1cm} (6)

Where U is the voltage of the cell (Volt), I is the current (A), t is the time of electrolysis (h), COD$_i$ and COD$_f$ are the initial and final values of COD (mg/l), and V is the solution volume (L).

In the present work effect of operating parameters like current density in the range of (5-25mAcm$^2$), pH in the range of 3-11, and NaCl addition in the range of ((0-2g/l) were investigated using one factor at one time as a research design. The purity of NaCl used in the present work was 99.5%.

3. Results and discussion

3.1 Effect of current density

Current density in comparison with other operating parameters has been recognized to be the most influential parameter on the effectiveness of an electrocoagulation process since it governs the rate of
aluminum ions dissolution from the anode into the solution [23]. The decay of COD with time at different values of current density is shown in Figure 2 using a solution having an initial COD of 425 ppm and a pH adjusted initially to 7 with the addition of NaCl at a level of 1g/l. Results showed that rising the current density results in lowering the final value of solution COD. It was found that the decline of COD with time goes down gradually. This behavior can be elucidated as the rate of anodic dissolution (Al) increases with increasing current density, causing a higher amount of precipitants and coagulants, leading to higher removal efficiency of the organic pollutants. Also rising the current density leads to an increase in the rate of bubble generation and decreases the bubble size leading to higher removal efficiency of organics by H₂ flotation combined with the coagulation effect [24].

![Figure 2: The decay of COD with time at different values of current density.](image)

[NaCl] = 1g/l, pH=7, Temp. = 25°C.

Table 2 displays the values of COD removal efficiency at different current densities. It was observed that the COD removal efficiency increases with rising the current density where COD removal efficiency higher than 98% could be obtained using a current density equal to 25 mAcm⁻² during 45 min. However, Energy consumption plays an essential parameter in the applicability of any approach of wastewater treatment. In this field, the value of electric energy is the most crucial feature in determining the economy of the electrocoagulation process [23]. Electric energy consumption (EC) is the quantity of electric energy required to eliminate a unit mass of the pollutant stream. As shown in Table 2, using higher current density leads to rising EC, because of increasing the losses of ohmic voltage in the cell. Results showed that EC increases to be higher than 27.78Kwh/Kg COD as the value of current density becomes higher than 15mAcm⁻² with a slight increase in COD removal efficiency; therefore, it is preferred to select this value of current density for further experiments. Analogous behaviors were observed in previous works [21, 25, 26, 27].

| Current density mA/cm² | COD Removal (%) at 45 min | EC (kWh/kg COD) |
|------------------------|---------------------------|-----------------|
| 5                      | 85.65                     | 5.15            |
| 10                     | 90.59                     | 14.66           |
| 15                     | 95.3                      | 27.78           |
| 20                     | 97.17                     | 40.86           |
| 25                     | 98.59                     | 55.94           |
As a general phenomenon, the pH of the medium altered during the operation of the process, and this change is based on the type of the anodic material as well as the initial value of pH. Nevertheless, the electrocoagulation system exhibits buffering behavior, mostly in alkaline conditions, avoiding large variations in the pH as well as reducing the efficiency of contaminant removal [28]. We observed experimentally that the pH during the experiments increased from 7 to be in the range of 7.4 to 8.1 based on the value of the current density, the lower value at higher current density. An analogous trend was detected by previous studies [29, 30, 31].

3.2 Effect of pH

Previous studies showed that aluminum ions be present in many forms and phases based on the pH and solution chemistry [25, 32]. For example, at pH values lower than (4), Al ions exist in the form Al(H₂O)₆³⁺, at pH values in the range between 5 and 6, they exist in the forms Al(OH)⁺² and Al(OH)₂⁺, at pH values in the range between 5.5 and 8.8, they exist in the form Al(OH)₃. When pH value increases to values higher than 8.8 Al dissolution as ions occurs again [26]. Figure 3 illustrates the decay of COD with time at various pH values using a current density of 15mA/cm² and adding NaCl at a concentration of 1g/l, while Table 3 represents the pH effect on the COD removal efficiency. Results showed that a decrease in COD removal efficiency occurs as the pH increases or decreases beyond (7), and COD removal efficiency with a maximum value could be obtained only at pH=7. Analogous observations were reported in previous works [21][25][26][27]. It was observed that pH increases experimentally during the electrolysis to be more alkaline related to the initial value. Similar behavior was perceived by previous works [27][29][30][31].

![Figure 3: Decay of COD with time at different values of pH.](image)

Table 3. Impact of pH on the efficiency of COD removal

| pH | COD Removal (%) at 45 min | EC (kWh/kg COD) |
|----|---------------------------|-----------------|
| 11 | 89.88                     | 30.5            |
| 9  | 91.76                     | 29.3            |
| 7  | 95.3                      | 27.78           |
| 5  | 88.2                      | 25.5            |
| 3  | 83.5                      | 24              |
3.3 Effect of NaCl addition

NaCl always adds to the solution as a supporting electrolyte because chloride ions have the ability to hinder the opposing effects of other anions, like SO$_4^{2-}$ and HCO$_3^-$). Briefly, the presence of carbonate ion can make precipitation of Ca$^{2+}$ or Mg$^{2+}$ ions as a coated film on the aluminum anode, causing an increase in the ohmic resistance of cell, followed by reducing the process effectiveness [33]. Figure 4 displays COD decay with time at various addition of NaCl using a value of 15mA/cm$^2$ for the current density and a value of 7 for the initial pH.

![Figure 4](image)

Figure 4. Decay of COD with time at various additions of NaCl.
Current density=15mA/cm$^2$, pH=7, Temp. = 25°C.

It was cleared that a decline in COD removal efficiency occurs as the addition of NaCl increases with a noticeable decrease in the energy consumption, as shown in Table 4. The increase of sodium chloride addition from 0 to 2 g/L results in a decline in the COD removal efficiency from 97.65% to 90.8% at the end of 45min. Results revealed that COD removal efficiency up to 98% could be obtained without the addition of NaCl, confirming that the originally existed chlorine ions in the petroleum refinery effluent play an addition role in degrading the pollutants via indirect anodic oxidation in combination with the major role of the Electrocoagulation. However, despite its role in preventing the formation of coated film of carbonate, using higher NaCl concentrations is not preferred due to the harmful effect of the chlorinated intermediate compounds that may be generated during the operation [34]. Table 4 shows that Increasing the NaCl addition decreased the EC due to the increase in the conductivity, which leads in turn to decrease the ohmic resistance of the solution (lower voltage cell). Using 1g/l as NaCl addition is recommended since lower energy consumption with removal efficiency higher than 95% could be obtained. Analogous behaviors were found in previous works [21, 25, 26].

| NaCl concentration (g/l) | Initial conductivity ($\mu$s/cm) | COD Removal (%) at 45 min | EC (kWh/kg COD) |
|--------------------------|---------------------------------|---------------------------|-----------------|
| 0                        | 5350                            | 97.65                     | 38.5            |
| 0.5                      | 5800                            | 96.7                      | 32.3            |
| 1.0                      | 6380                            | 95.3                      | 27.78           |
| 1.5                      | 7030                            | 92                        | 27.1            |
| 2.0                      | 7500                            | 90.8                      | 26.72           |

Table 4. Impact of NaCl addition on the efficiency of COD removal
4. Conclusions
In this study, applying an electrocoagulation process to treat Al-Muthanna petroleum refinery wastewater has been achieved successfully. The impacts of different operating factors like current density, NaCl addition, and pH on the COD removal from this wastewater were examined in detail. The most essential and crucial factor in the present work was the current density followed by pH. While the addition of NaCl enhanced the economy of the process by decreasing the needed energy consumption in addition to its effect on hindering the carbonate formation on the anode. An adverse effect on the COD removal efficiency was observed with increasing NaCl concentration. It can be concluded that starting the electrocoagulation process with an initial pH value of (7) is preferred since most of the Al ions existing as Al (OH)\textsubscript{3} form. An acceptable removal efficiency of COD(95.3%) with an energy consumption of (27.78kWh/kg COD) could be obtained during 45 min when a current density of 15 mA cm\textsuperscript{-2} is applied with NaCl addition at a concentration of 1 g/ and regulating the pH to be (7). Combining the present method with an electrooxidation approach may be a promising step for getting better treatment efficiency at lower time and energy consumption.

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