

# Treatment of Petroleum Refinery Wastewater by Continuous Electrocoagulation

Muftah H. El-Naas, Sulaiman Al-Zuhair, Amal Al-Lobaney  
*Chemical and Petroleum Engineering Department, UAE University*

## Abstract

*Electrocoagulation is a process that involves dissolution of a metal anode with simultaneous formation of hydroxyl ions and hydrogen gas at the cathode. It has recently attracted the attention of many industries as a potential technique for the treatment and purification of several types of highly contaminated wastewater. In this study, electrocoagulation has been evaluated as a treatment process for the reduction of high concentrations of COD in petroleum refinery wastewater. Experiments were carried out in the continuous mode using an electrocoagulation reactor with aluminum electrodes. The effects of key operating parameters such current density, pH, initial COD content and the inlet flow rate were investigated. The reduction of COD content was significantly improved by increasing the current density and reducing the feed flow rate. The reactor performance was optimized at a neutral pH, in the range of 6-8, and ambient temperature of about 25 °C. The results demonstrated the technical feasibility of electrocoagulation for the pretreatment of heavily contaminated industrial wastewater.*

**Keywords:** COD reduction; aluminum electrodes; Petroleum refinery wastewater; Current density; Pretreatment

## 1. Introduction

The treatment of wastewater, generated by the industry, represents a significant environmental pollution challenge, because of its large quantity and the diversity of pollutants present [1]. One of these industries is the petroleum refinery, which produces considerable amounts of wastewater with high concentrations of aliphatic and aromatic hydrocarbon that usually have detrimental and harmful effects on plant and aquatic life, as well as the surface and ground water sources [2]. Therefore, effective and

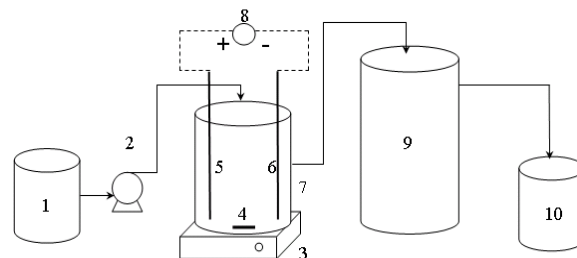
feasible methods for treating petroleum refinery wastewater are needed. These methods may include biodegradation, ultrafiltration, adsorption, coagulation, and electrochemical processes [2]. Electrochemical techniques such as, electroflotation (EF), electrodecantation (ED), electrocoagulation (EC), and electrokinetic remediation have the advantage of being easily distributed, and require minimum amount and number of chemicals. In recent years, several studies have focused on electrocoagulation, which is an effective process used to treat wastewaters with finely dispersed particles [3]. This technique is robust and compact, and hence has the potential to replace sophisticated processes that require large volumes and/or number of chemicals [4]. Electrocoagulation is a primary technique for treatment of various wastewaters generated by industry, agriculture or urban areas. The technique relies upon the electrochemical dissolution of sacrificial Al or Fe electrodes. The generated cations contribute to the reduction of the stability of suspended entities contained by reducing their zeta potential [5]. In addition, upon formation of hydroxides ions at the cathode, metal ions form complexes with iron or aluminum hydroxides, which are known to be efficient coagulants. Furthermore, the hydrogen bubbles formed at the cathode adsorb the flocs formed by the process, and ensure their flotation, which simplifies their separation from the treated water [5]. The electrocoagulation technique have been considered for the treatment of wastewaters in a very broad range in terms of nature and composition, such as: wastewater from textile industry [1, 5-7], oil suspension [8, 9], petrochemical industry wastewater [2], wastewater containing arsenic [10 ], phenolic compounds [11, 12], heavy metals [13, 14] and Fluorides [15, 16]. In spite of the considerable success of electrocoagulation for the treatment of various types of wastewater, its application as a possible technique for the treatment of petroleum refinery wastewater is

rather scarce in the literature. A preliminary evaluation of a batch electrocoagulation reactor proved to be effective for the treatment of refinery wastewater [2]. The main objective of the present study, therefore, is to evaluate the potential of continuous electrocoagulation of refinery wastewater and to examine the effect of different operating parameters on the reactor performance.

## 2. Experimental Setup

Experiments were carried out in 1500 ml cylindrical reactor (14 cm diameter × 10 cm length). Electrode assembly is the heart of any electrochemical treatment facility. Therefore, appropriate selection of electrode material is very important [17]. The effectiveness of using aluminum, iron and stainless steel electrodes in different cathode and anode arrangement to treat the petroleum refinery wastewater was investigated. The results, presented in the batch study, showed that the aluminum electrode is more capable to treat such wastewater [2]. Therefore, in the present study aluminum electrode was used. The aluminum plates with different effective working areas in the range of 20 – 50 cm<sup>2</sup> were tested. The electrodes of the electrochemical cell were connected to an electrical DC power supply (PE-23005 POPULAR). The distance between the anode and the cathode was kept constant at 7.5 cm.

The wastewater samples were collected from a specified location in the wastewater treatment system of a local petroleum refinery. The samples had a dark green color, a very strong pungent odor and had high concentrations of COD and total phenols. Characteristics of the wastewater samples are presented in Table 1. A 600 ml of the wastewater was treated in batch operation for one hour and then the continuous operation was started by pumping the wastewater to the reactor by a peristaltic pump (GILSON Miniplus 3) with different flow rates in the range of 5 -15 ml/min. The effluent was then sent to a settling tank, which has double the volume capacity of the electrocoagulation reactor. Samples were periodically withdrawn directly from the reactor medium and after the settling tank. The COD of the withdrawn samples was measured using HACH UV spectrophotometer (Model DR-5000). The experimental setup of the continuous electrocoagulation process is shown in Figure 1.



**Figure 1.** A schematic diagram of the electrochemical apparatus.(1) Feed tank, (2) Feed pump, (3) Magnetic stirrer, (4) Magnetic bar, (5) Anode, (6) Cathode, (7) Electrocoagulation reactor, (8) DC power supply, (9) Settling tank and (10) Product tank

**Table 1. Characteristics of wastewater**

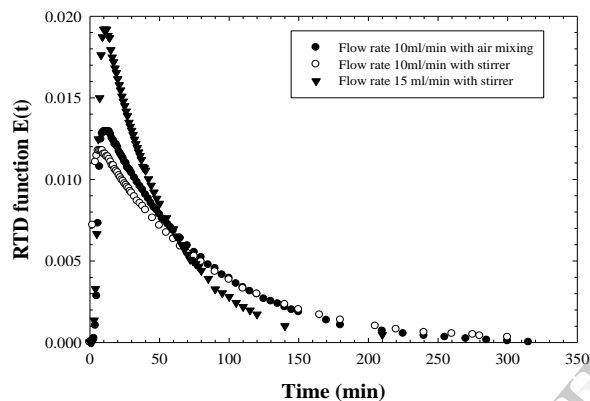
Parameter	Value
pH	8.3-8.9
Conductivity (mS/cm)	5.2-6.8
Total Suspended Solid (g/l)	0.03-0.04
Total Dissolved Solid (g/l)	3.8-6.2
SO <sub>4</sub> (mg/l)	14.5-16
COD (mg/l)	3600- 5300
Total Phenols (mg/l)	160-185
Phenol (mg/l)	11-14
o-Cresol (mg/l)	14-16.5
m,p-Cresol (mg/l)	72-75
N-Hexane (mg/l)	1.8-1.85

## 3. Results and Discussion

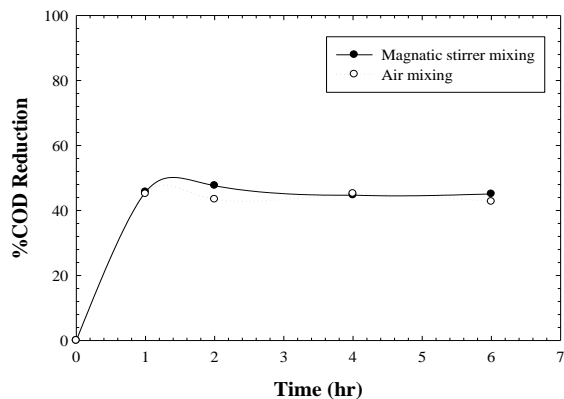
### 3.1 Effect of mixing mechanism

The actual residence time in the electrocoagulation reactor must be determined, before the start of the experimental work. Therefore, a residence time distribution (RTD) experiment was carried out by injecting 8.5 ml of NaOH as a pulse into the inlet stream to the reactor and the conductivity of the exit stream was measured with time. The residence time was then determined from dividing the working volume by the volumetric flow rate. The effect of using air bubbling and magnetic stirring as two mixing techniques at two different liquid flow rates is shown in Figure 2. It was found that, at the same inlet flow rate of 10 ml/min, the type of mixing had almost negligible effect on the reactor RTD. At an inlet flow rate of 10 ml/min, the mean residence times using air bubbling and magnetic stirring were 70 and 73.2 min, respectively. The effect of the two types of mixing

techniques, namely air bubbling and magnetic stirrer, on the performance of the EC cell was also evaluated. The COD removal during the continuous operation with a current density of  $33 \text{ mA/cm}^2$ , initial  $\text{pH} = 7.8$  and initial temperature =  $25^\circ\text{C}$  is shown in Figure 3. The results clearly show that the mixing mechanism has an insignificant effect on the reduction of COD. However, it was observed that the sludge produced using air mixing settled faster than that produced with the magnetic stirrer. This is due to the enhanced floatation effect by air bubbling, removing the oily component of the wastewater and hence reducing time for settling of the generated sludge. Therefore, in all subsequent experiments, air mixing was selected as the preferable mixing technique.



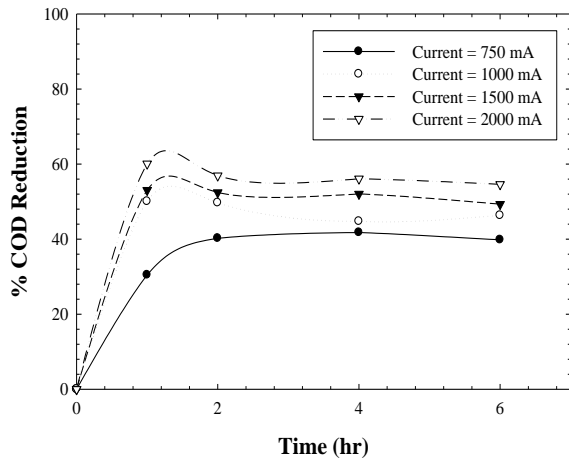
**Figure 2.**RTD function,  $E(t)$ , with time for different flow rates and types of mixing



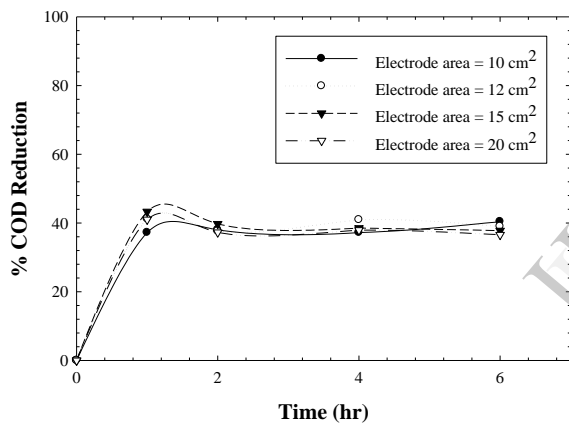
**Figure 3.**Effect of mixing type on the COD removal. Current density =  $33 \text{ mA/cm}^2$ , initial  $\text{pH} = 7.8$ , initial concentration =  $5064 \text{ mg/l}$ , initial temperature =  $25^\circ\text{C}$  and flow rate =  $10 \text{ ml/min}$

### 3.2 Effect of current density

It is well-known that current density not only determines the coagulant dosage rate but also the bubble production rate and size and the flocs growth, all of which can influence the treatment efficiency of the electrocoagulation [18-19]. Current density, which is defined as the ratio of applied current over the effective area of the electrode, increases with increasing the applied current and/or decreasing the area. The effect of current density by changing the current while keeping the effective area constant at  $50 \text{ cm}^2$ , on the percentage removal of COD is shown in Figure 4. The results show that the steady state was reached after about 1 hr. This indicates that the system has reached the steady state after the batch period of the experiment, and during the continuous part, the reduction of COD remained constant at the steady state value. Similar behavior was observed in all continuous experiments. It can clearly be seen that the COD reduction enhanced by increasing the current density. The removal percentage increased from 39% to 57 % by increasing the current from  $750 \text{ mA}$  (current density =  $15 \text{ mA/cm}^2$ ) to  $2000 \text{ mA}$  (current density =  $40 \text{ mA/cm}^2$ ). This is expected, as by increasing the current, the anode dissolution rate increases, which in turn increases the concentration of metal ions in the solution, and consequently the pollutants removal rate is enhanced [2]. In addition, an increase in bubble density occurs at high current, which also results in a greater flux and faster removal of pollutants [2, 20]. To further understand the effect of current density, the COD removal was tested at different current densities, varied by changing the electrode area, while keeping the applied current constant. It can be seen from Figure 5 that the percentage of COD reduction in this case was not affected. Increasing the electrode area results in reduction in current density, and hence decreases the amount of aluminum hydroxide produced, which should result in lowering the efficiency of COD reduction. However, at the same time this increase in the electrode area increases the overall electrolysis reaction effective area, which has a positive effect on the COD reduction. It seems then that the two opposing factors cancel each other, which results in the insignificant effect of electrode area as shown in Figure 5.



**Figure 4.**Effect of current on the COD removal. Electrode area =  $50\text{cm}^2$ , initial pH =7.8, initial concentration =  $5064\text{ mg/l}$ , initial temperature =  $25^\circ\text{C}$  and flow rate =  $10\text{ ml/min}$

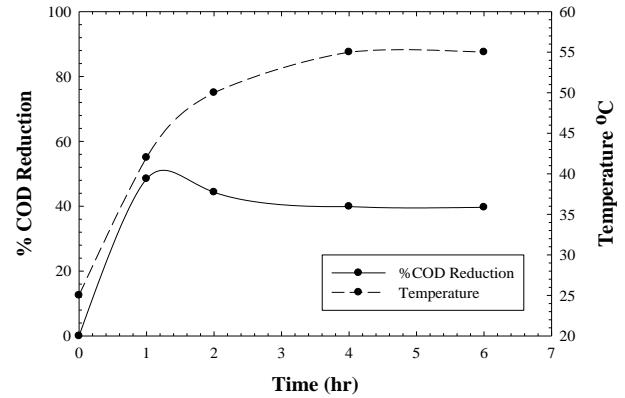


**Figure 5.**Effect of electrode area on the COD removal. Current =  $600\text{ mA}$ , initial pH =7.8, initial concentration =  $5064\text{ mg/l}$ , initial temperature =  $25^\circ\text{C}$  and flow rate =  $10\text{ ml/min}$

### 3.3 Effect of temperature

In Figure 4, it was noted that the removal percentage slightly dropped after the batch period. This may be due to the increase in temperature during the electrolysis reaction. To understand this phenomenon, the temperature was monitored throughout the course of the experiment using a current of  $2000\text{ mA}$ . It can be seen from Figure 6 that during the batch period of the experiment, the reduction of COD reach  $48\%$  and the temperature increased to reach  $42^\circ\text{C}$ . After about 4 hours of operation, the temperature reached  $55^\circ\text{C}$  and the COD reduction stabilized at  $40\%$ . The increase in

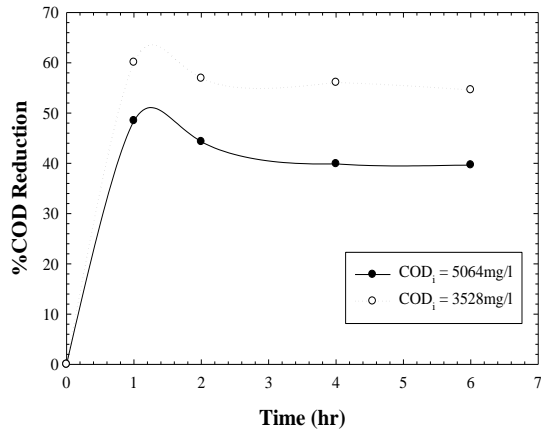
temperature caused an increase in the solubility of aluminum hydroxide, which is responsible for removing the colloidal particles, and hence reducing the electrolysis efficiency.



**Figure 6.**Percentage COD reduction with time. Current =  $2000\text{ mA}$ , electrode area =  $50\text{ cm}^2$ ; initial pH =7.8, initial concentration =  $5064\text{ mg/l}$ , initial temperature =  $25^\circ\text{C}$  and inlet flow rate =  $10\text{ ml/min}$

### 3.4 Effect of initial concentration

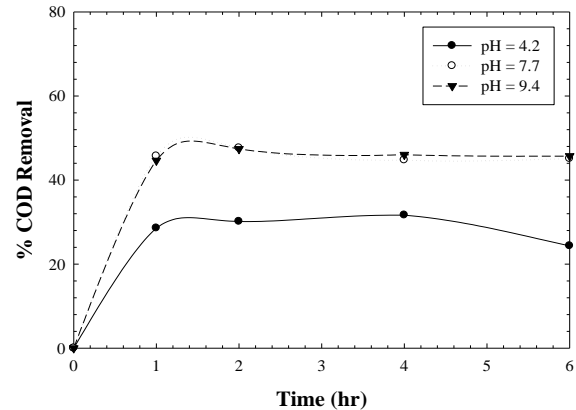
The initial concentration of COD in the wastewater samples differ from time to time according to disturbances inevitably occurred during the processing. The effect of the initial COD concentration on the percentage reduction of pollutants was determined for two samples collected from the same location, but at different times. Figure 7 shows that the sample with high initial concentration has a lower COD percentage removal. This is due to the fact that the amount of aluminum hydroxide is constant for both cases, which mainly depends on the current density and electrode material, and is independent of the initial concentration of the contaminants in the wastewater. Since the operating conditions of both cases were kept the same, similar amounts of COD were removed, and hence, lower percentage reduction resulted for the higher initial concentration sample.



**Figure 7.**Effect of initial concentration on the COD removal. Current = 2000 mA, electrode area = 50 cm<sup>2</sup>, initial pH = 7.8, initial temperature = 25°C and flow rate = 10 ml/min.

### 3.5 Effect of pH

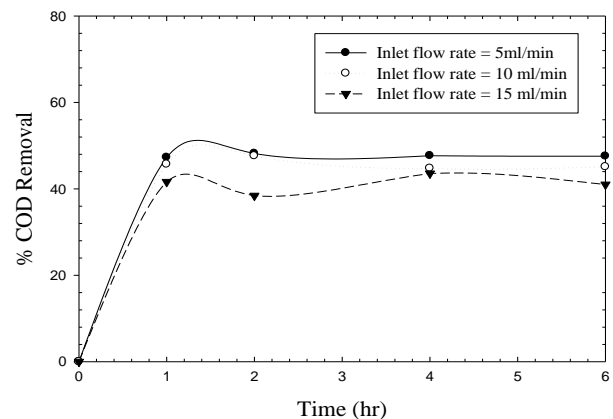
The value of pH is an important factor that affects the performance of electrochemical and chemical processes. The COD removal was examined at pH values of 4.2, 7.7, and 9.4, adjusted by using HCl or NaOH (0.1 M). Figure 8 shows that the COD removal increases with increasing the pH up to about 8, after which it becomes constant. The drop in the COD reduction at low pH values is in agreement with the amphoteric chart of aluminum hydroxide Al(OH)<sub>3</sub> that precipitate at pH 6-7 and its solubility increases as the solution becomes more acidic [21-23]. Increasing the precipitation of the Al(OH)<sub>3</sub> tends to increase the amount of colloidal particle that is removed with the Al(OH)<sub>3</sub>. The solutions pH increases during the electrocoagulation experiments due to the cathodic reaction, given in Eq (1), which takes place during electrocoagulation [24]:



**Figure 8.**Effect of pH on the COD removal. Current density = 33 mA/cm<sup>2</sup>, initial concentration = 5064 mg/l, initial temperature = 25°C and inlet flow rate = 10 ml/min

### 3.6 Effect of inlet flow rate

The removal efficiency of COD was studied using different flow rates in the ranges 5–15 ml/min at constant current density of 33 mA/cm<sup>2</sup>. At the same current densities, it was shown that when the flow rate increased, the COD removal efficiency decreased, as shown in Figure 9. The COD reduction efficiency dropped from 48 to 41 % as the flow rate increased from 5 to 15 ml/min. This is expected since higher flow rates lead to lower retention time, and hence the pollutants spent less time in the reactor and its reaction with Al(OH)<sub>3</sub> would not be complete. However, this decline in the COD reduction efficiency is not significant given that the flow rate had been tripled.



**Figure 9.**Effect of inlet flow rate on the COD removal. Current density = 33 mA/cm<sup>2</sup>, initial pH = 7.8, initial concentration = 5064 mg/l and initial temperature = 25°C

## Conclusions

Electrocoagulation was assessed as a possible technique for the reduction of COD concentration in petroleum refinery wastewater. Wastewater samples containing two different COD concentrations (3628 to 5064 mg/l), collected from a specific location in the wastewater treatment system of a local petroleum refinery, were treated in a continuous electrochemical cell using aluminum electrode. The effects of current density, initial pH and inlet flow rate were investigated. At optimum conditions, it was shown that electrocoagulation can achieve percentage reduction of up to 57 % of the COD.

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