



Treatment of synthetic petroleum refinery wastewater in a continuous electro-oxidation process

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Received 5 October 2012; Accepted 8 January 2013

ABSTRACT

A continuous electrochemical process was investigated for the treatment of synthetic petroleum refinery wastewater. Phenol, crude oil, and kaolin were added in concentrations typical to that found in a refinery wastewater to simulate the soluble, immiscible, and colloidal phases, respectively. Stainless steel (AISI 304) electrodes were used in the electrochemical cell, while an immersed ZW-1 ultrafiltration membrane module was utilized for solid–liquid separation. Different operational conditions were investigated by varying current density and contact time. The optimum current density was noted to be 30 mA cm^{-2} with 20 min of contact time. Tap water having a conductivity of $5,000 \mu\text{ohm/cm}$ was used as for the preparation of the synthetic wastewater. The results from series of experiments showed that high total dissolved solids (1,300 mg/L) in raw water produced a significant interference in degradation of phenol. However, a removal efficiency of 99 percent was achieved for turbidity, while oil was below the minimum detection limit of 1.4 mg/L for the EPA method 1664 used to detect oil in the treated samples.

Keywords: Electro-oxidation; Current density; Stainless steel electrodes; Petroleum wastewater; Phenol; Oil

1. Introduction

An increased understanding of the environmental requirements of petroleum industry advocates the necessity of constant enhancements in the current treatment technologies, along with the exploration of new technologies for various types of petrochemical effluents. Traditional treatment processes of wastewater effluents discharged by petroleum refineries are usually based on the mechanical, physicochemical, and biological methods.

Electrochemical and membrane filtration processes are wastewater treatment technologies that are currently experiencing both increased recognition and considerable technical improvements. To the knowledge of the authors, a combined use of both these technologies for the treatment of various types of industrial wastewater is in the initial phase of research.

The characteristics of petroleum industry wastewater are highly industry-specific, that is, the petroleum product manufactured at the plant. Therefore, wastewater from a petroleum plant has to be extensively

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characterized before deciding the viable technology for the treatment or reuse.

In this study, the treatment of synthetic wastewater with the characteristics of a typical petroleum industry effluent was investigated. Such wastewater usually contains three phases of pollutants, namely solids and colloids, immiscible (oil and grease), and soluble (organic and inorganic).

Phenol is a common component of wastewater that may enter the environment from petroleum refineries, coal conversion plants, and municipal waste treatment plant discharges. It can pose severe health hazards and should be handled with extreme caution. Processes proved to be effective in the treatment of phenol include Fenton [1], Photo-Fenton [2], Ozonation [3], Wet air oxidation [4], and also Ti/SnO₂-Sb anode [5].

Almost all refineries produce various types of oil and organosulfur compounds in their wastewaters [6]. The oil and grease in industrial wastewater may appear as free oil, dispersed oil, emulsified oil, soluble oil or as a coating or suspended matter. Oily wastes discharges may have objectionable odors, cause undesirable appearance, burn on the surface of receiving water-creating potential safety hazards, and consume dissolved oxygen necessary to forms of aquatic life. In greater quantities, it limits oxygen transfer [7]. Conventional coagulation using chitosan, starch, alum, and ferric chloride in combination with air flotation have been found out to be effective for the removal of oil from wastewater [8]. Electrocoagulation is also reported as a promising technology for the removal of oil from wastewater [9,10].

Kaolinite [Al₂Si₂O₅(OH)₄] mixed with water may form a hydrophilic colloidal suspension because of its mineral origin. The presence of colloidal material in water causes high turbidity in wastewater. Turbidity itself is not a major health concern and poses a minimal direct health risk, but high turbidity in wastewater can interfere with disinfection processes. The most common method used to remove turbidity caused by colloidal particles is the use of coagulation along with flocculation. Various coagulants such as aluminum sulfate, ferric sulfate, and also various polymers such as polyacrylamide are commonly used for this purpose [11]. Various advanced treatment processes, such as ultrafiltration and electrocoagulation, are also proved to be efficient for the treatment of wastewater with high turbidity caused by the presence of colloidal material in wastewater [12].

The passage of current by means of electrodes generates *in situ* coagulants by dissolving either aluminum or iron ions from aluminum or iron electrodes, respectively [13]. Stainless steel electrode

predominantly releases Fe²⁺ ions. The metal ions generation takes place at the anode, while hydrogen gas is released from the cathode. The chemical reactions taking place at the electrodes are given as follows.

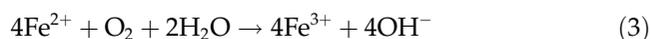
For Stainless steel anode:



at alkaline conditions;



at acidic conditions;



In addition, there is oxygen evolution reaction;



For stainless steel cathode;



Electrocoagulation has been proven to be effective in water treatment such as drinking water supply for small or medium sized community, marine operations and even for boiler water supply for industrial processes where a large water treatment plant is not economical or necessary [14]. It has also been found efficient in removing oil and greases [15]. It is also used as a pretreatment process for the removal of viruses through membranes [16].

The use of electrocoagulation in the treatment of wastewater containing coloring materials [17], suspensions of ultra-fine particles [18], boron [19], nitrate [20], fluoride [21], arsenic [22], chemical mechanical polishing wastewater [23], tannery effluents [24], and laundry wastewater [25] was reported to be efficient. Additionally, electrocoagulation was found particularly successful in treating domestic wastewater treatment [26], municipal sewage [27], oil-water emulsion [28], and natural organic matters (NOMs) from wastewater [29]. More recent work on the degradation of phenol using electrochemical processes can be cited in the study described by Yoon et al. [30], Cesarino et al. [31], Liu et al. [32], Sun et al. [33], Huang and Chu [34], Moore et al. [35], Muna et al. [36], Zhang et al. [37], Arvinte et al. [38], Azevedo et al. [39], Wei et al. [40], Chen et al. [41], Cui et al. [42], Chen et al. [43], Santos et al. [44], and Qu et al. [45].

Ultrafiltration has been used to remove humic acids from wastewater [46], heavy metal from

polluted wastewater [47], carboxylic acids [48], and to treat textile effluent pollutants [49]. Removal of heavy metals from simulated groundwater using enhanced ultrafiltration has also been reported to be efficient [50].

Submerged ultrafiltration modules are successfully tested in combination with biological treatment for the treatment of municipal wastewater [51], food processing wastewater [52], and tannery wastewater [53]. At present, the use of immersed membrane processes in the treatment of various types of wastewater is extensively investigated.

Chemical coagulation has been used in combination with ultrafiltration to treat humic substances from highly colored water [54] and also for direct potable water treatment [55]. The combination of electrocoagulation with ultrafiltration is a new area of research and recently published works have emerged [56–63].

Based on the above-mentioned discussion, the main objective of this study is to investigate the use of an electrochemical process in treating synthetic petrochemical wastewater under continuous flow scheme.

2. Materials and methods

Table 1 shows the typical concentration range of pollutants in petroleum refinery wastewater that is used as a reference for the preparation of the synthetic wastewater for this study. Oil was entirely emulsified through blending, and no free oil droplets were observed on the surface of the synthetic wastewater. To synthesize the wastewater, kaolin was used to form turbidity, crude oil was used to form oil and standard phenol solution was used to form phenol.

The experimental setup consists of a tank with two chambers, namely the electrochemical chamber and membrane chamber that are separated by a plexiglas wall, as shown in Fig. 1. Stainless Steel was used for

both anode and cathode. The electrodes were connected to a DC power supply with galvanostatic operational options for controlling the current density. A distance of 30 mm between anode and cathode was maintained throughout the investigation.

Commercial AISI 304 stainless steel sheets were used as the electrode material in this work. The stainless steel was degreased with alcohol, cleaned with deionized water, and dried in oven at 103°C. The electrodes dimensions were 100 × 40 × 2 mm.

Zenon (ZW-1) immersed bench scale module was used as the ultrafiltration membrane. The average pore size for the membrane was 0.04 μm. The configuration of the module was outside/in hollow fiber with nominal membrane surface area of 0.047 m².

A magnetic stirrer was used to continuously mix the feed that was drawn through a pump from the synthetic wastewater supply tank in the electrochemical chamber. Adjusting the flow rate from the supply tank was used to control the contact time. The wastewater was introduced at the bottom of the electrochemical chamber to minimize short-circuiting of flow.

A suction pump was used to apply the required pressure on the submerged membrane and maintain the permeate flux of the treated wastewater that should be equal to the influent of wastewater to the electrochemical chamber. A hopper was provided at the bottom of the submerged membrane chamber to collect and remove the produced sludge.

In the continuous flow experiments, phenol solution was constantly introduced into the electrochemical chamber. A phenol molecule introduced to electrochemical treatment is expected to spend a time equal to the contact time set for the particular experiment in electrochemical cell, which is controlled through the flow rate (Q) of the system.

The continuous feed flow required to maintain a particular contact time in the electrochemical chamber was calculated the following equation.

$$Q = V/t \quad (6)$$

where

- Q = influent to the electrochemical cell (ml/min)
- V = volume of chamber (500 ml)
- t = contact time (min)

In the initial phase, sixteen experiments were performed resulting from all the possible permutations of four current densities (5, 10, 30, and 50 mA cm⁻²) and four contact times (5, 10, 20, and 30 min). No electrolyte was added in these experiments, because the raw

Table 1
Characteristics of typical and synthetic petroleum refinery wastewater

Parameters	Typical range	Synthetic wastewater
pH	6.2–7.6 ^a	6.5
Conductivity, μmhos/cm	746–925 ^a	4,000
Turbidity, NTU	60–100 ^a	100
Phenol ^b , mg/L	67–68 ^b	75
Oil and grease ^c , mg/L	1.96–2.00 ^c	10

Sources: ^a[64], ^b[65], ^c[66].

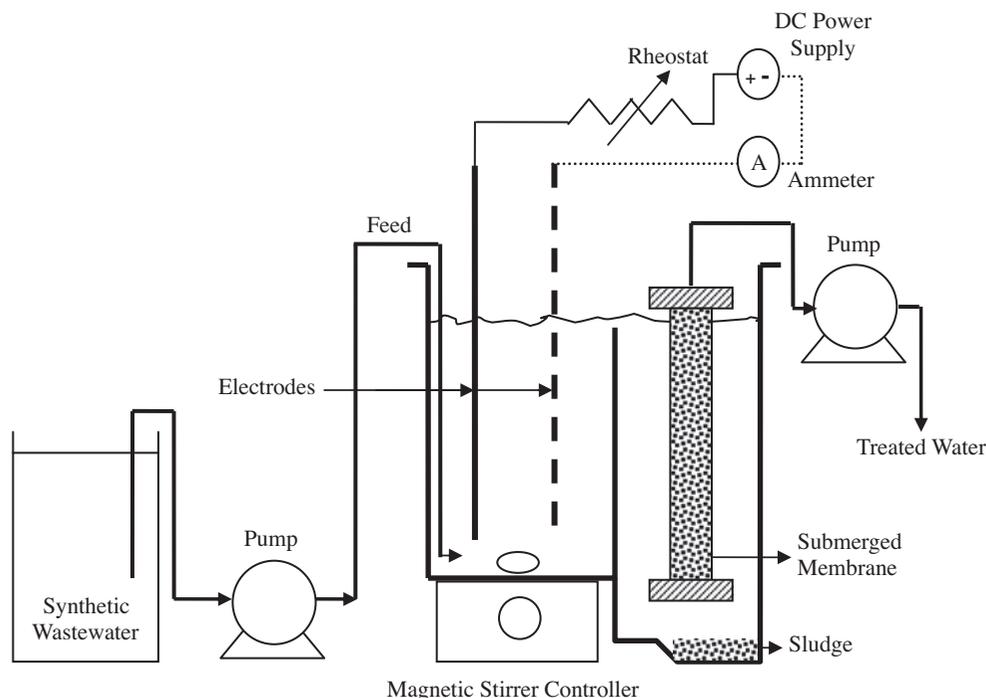


Fig. 1. Schematic diagram of combined electrochemical-ultrafiltration process.

water used for preparing the synthetic wastewater contained high amount of total dissolved solids (TDS = 1,300 mg/L). The optimum current density established by these sixteen experiments was used in combination with all four contact times that were investigated in the initial phase. These experiments were performed to study the effect of kaolin in the system, particularly, when a white coating was observed to form on the cathode during initial phase of experiments.

Similarly, additional four experiments were performed to investigate the effect of periodic current reversal on the process performance. In one of the experiments, deionized water was used in the preparation of the synthetic wastewater. In this experiment, only phenol was used to prepare the synthetic wastewater, because earlier experiments suggested an influence of tap water on degradation of phenol. Table 2 summarizes the design of experiments adopted for this study. It is worth mentioning that each experiment was repeated 2–3 times depending on the reproducibility and only average values were reported in the results.

Standard curve for phenol in UV-Spectrophotometer was established by observing absorbance peaks at 270 nm for five different concentrations of phenol, namely 1, 10, 50, 75, and 100 mg/L. It is worth mentioning that a new calibration curve was constructed each time an experiment was performed.

3. Results and discussion

Effluent samples from the electrochemical chamber were collected and analyzed for phenol to obtain a degradation profile at different operating parameters. The concentration of phenol detected at various time intervals, during an experimental run of 120 min at current densities of 5, 15, 30, and 50 mA cm⁻², with various contact times are demonstrated in Figs. 2–5, respectively.

Fig. 2 clearly shows that at 5 mA cm⁻² and 5 min of contact time, phenol reached the lowest concentration of 63 mg/L at 120 min of sampling time. It is worth to mention that phenol concentration in the influent was 75 mg/L. Moreover, the figure demonstrates that as the contact time was increased, the concentration of phenol was decreased insignificantly. The lowest phenol concentration was observed to be 55 mg/L for a contact time of 30 min which is equivalent to a removal efficiency of 27%.

Fig. 3 shows the concentrations of phenol achieved at a current density of 15 mA cm⁻² and different contact times. Phenol concentrations were noted to be lower when compared to those observed at a current density of 5 mA cm⁻², particularly in the first 10 to 20 min of sampling time. The lowest phenol concentration was observed to be 49 mg/L at sampling and contact time of 20 and 10 min, respectively. The lowest concentrations obtained at 5, 20, and 30 min of contact

Table 2
Design of experiments

Exp. no.	Oil & grease (mg/L)	Phenol (mg/L)	Suspended solids (mg/L)	Current density (mA cm ⁻²)	Contact time (min)	NaCl conc. (mg/L)
<i>Raw water as base solvent</i>						
1	10	75	100	5	5	0
2	10	75	100	5	10	0
3	10	75	100	5	20	0
4	10	75	100	5	30	0
5	10	75	100	15	5	0
6	10	75	100	15	10	0
7	10	75	100	15	20	0
8	10	75	100	15	30	0
9	10	75	100	30	5	0
10	10	75	100	30	10	0
11	10	75	100	30	20	0
12	10	75	100	30	30	0
13	10	75	100	50	5	0
14	10	75	100	50	10	0
15	10	75	100	50	20	0
16	10	75	100	50	30	0
<i>Raw water as base solvent (no kaolin added)</i>						
17	0	75	100	30 (Optimum)	5	0
18	0	75	100	30 (Optimum)	10	0
19	0	75	100	30 (Optimum)	20	0
20	0	75	100	30 (Optimum)	30	0
<i>Raw water as base solvent (periodic reversal in current direction)</i>						
21	10	75	100	30 (Optimum)	5	0
22	10	75	100	30 (Optimum)	10	0
23	10	75	100	30 (Optimum)	20	0
24	10	75	100	30 (Optimum)	30	0
<i>Deionized water as base solvent</i>						
25	0	75	0	30 (Optimum)	20 (Optimum)	4,000

time were 55, 63, and 62 mg/L, respectively. The maximum removal efficiency achieved using this current density was only 35%.

Fig. 4 shows the concentrations of phenol observed at a current density of 30 mA cm⁻² and different contact times. The figure indicates that phenol concentrations at 10 min of sampling time were 12, 34, 0, and 24 mg/L for the contact times of 5, 10, 20, and 30 min, respectively. This figure also shows that there is a clear pattern for significant removal of phenol in the initial 20 min that failed to continue throughout the period of the experiment. It is interesting to note that no phenol was detected at a contact time of 20 min giving an indication of complete electro-oxidation of phenol.

The effect of contact time on the degradation of phenol at a current density of 50 mA cm² is shown in Fig. 5. The figure clearly shows that phenol concentrations in samples collected after 10 min of experiment run were 26, 56, 21, and 1 mg/L for the contact times of 5, 10, 20, and 30 min, respectively. A significant removal of phenol continued for the first 40 min of sampling time. Phenol concentrations observed after 40 min of experimental run were 58, 60, 51, and 38 mg/L, suggesting a maximum of 49 percent of phenol removal efficiency at this sampling time. It is worth to mention that such significant removal was observed only during first 20 min of the experiment for the current density of 30 mA cm².

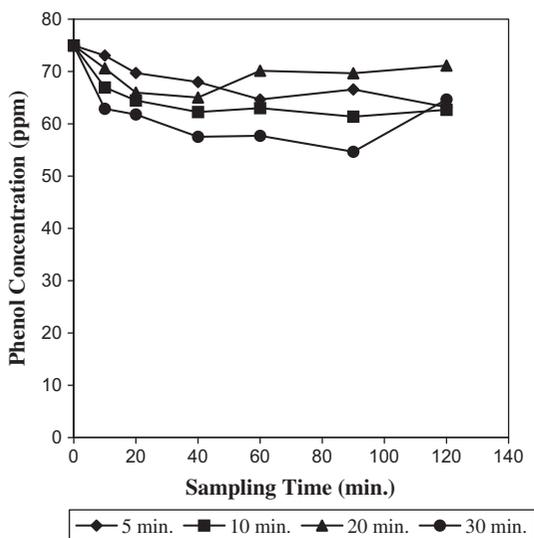


Fig. 2. Effect of contact time on the degradation of phenol at a current density of 5 mA cm^{-2} .

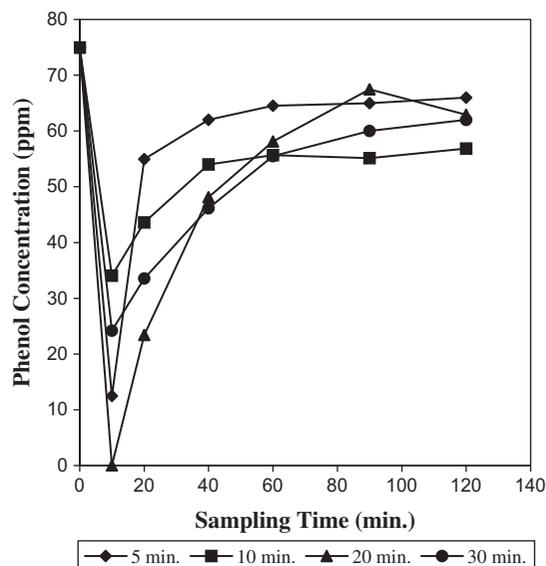


Fig. 4. Effect of contact time on the degradation of phenol at a current density of 30 mA cm^{-2} .

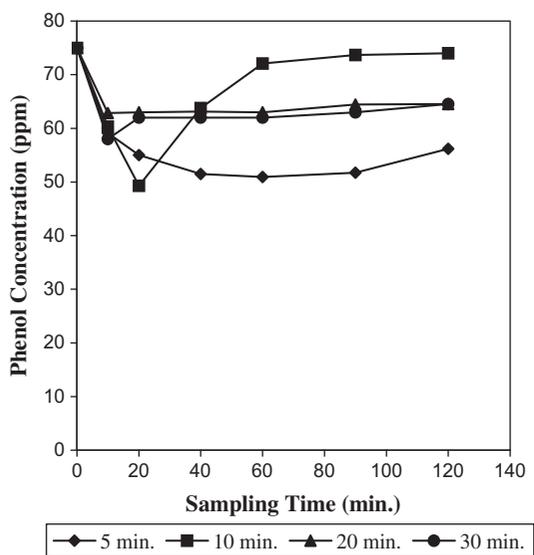


Fig. 3. Effect of contact time on the degradation of phenol at a current density of 15 mA cm^{-2} .

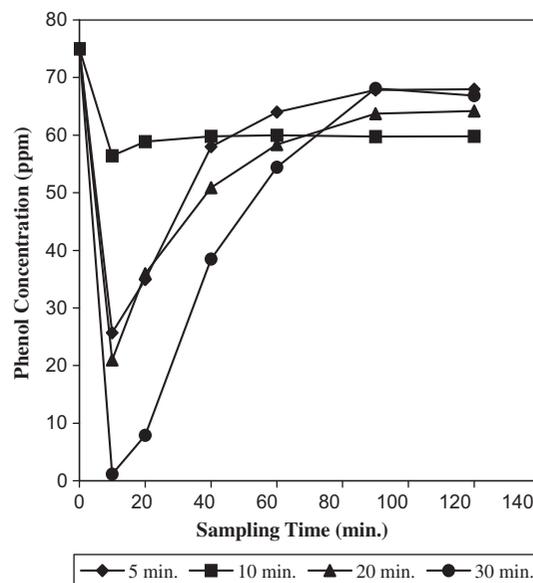


Fig. 5. Effect of contact time on the degradation of phenol at a current density of 50 mA cm^{-2} .

Figs. 2–5 show an apparent relationship between current density and phenol degradation. As current density was increased, the concentration of phenol in the effluent of the synthetic wastewater was found to decrease, which can be attributed to the electroredox reactions taking place within the electrochemical cell. The figures clearly indicate that phenol removal efficiency reached 100% at a current density of 30 mA cm^{-2} and contact time of 10 min. The figures also show that phenol concentration started to increase after 10 min of experimental run and remained so throughout the

experimental period. Factors that could have caused hindrance in the degradation of phenol after 20 min of experimental run will be discussed in the following section.

In all experiments that were discussed previously, a white coating was observed to form on the cathode throughout the experimental run. The amount of coating was observed to be more for higher current densities. No similar observations were reported in the published literature that was reviewed. Based on

such results, the discontinuity in phenol degradation was attributed to the formation of the coating. It was assumed that such coating could have hindered the process of phenol degradation. Since raw water with high TDS was used in preparation of the synthetic wastewater, the white coating could have originated from salts present in the raw water. Another reason that could have caused the formation of the white coating is the use of kaolin as a suspension to form turbidity in the synthetic wastewater. To investigate the probable reasons for the hindrance of phenol degradation, several experiments were conducted.

To investigate the effect of kaolin on the performance of the process, the synthetic water was prepared without kaolin and was treated at optimum operating conditions (current density of 30 mA cm^{-2} and detention times of 5, 10, 20, and 30 min). Fig. 6 shows the effect of contact time on phenol degradation at 30 mA cm^{-2} of current density when kaolin was not used. Comparing results obtained in Fig. 4 (wastewater with kaolin) with those obtained in Fig. 6 (wastewater without kaolin), it is evident that kaolin had no effect on the process performance, since both figures present almost similar results. As an example, samples collected after 10 min of experimental time showed that phenol concentrations were 12, 34, 0, and 24 mg/L for contact times of 5, 10, 20, and 30 min, respectively, when kaolin was added in synthetic wastewater (Fig. 4). In the other experiment, when kaolin was not used, phenol concentrations obtained under similar operating conditions were 15, 32, 2, and

22 mg/L (Fig. 6). Moreover, at the end of all experiments, the same white coating was found to form on the cathode.

Next, a set of experiments were performed with the periodic reversal in current direction. The reason for these experiments was to investigate the effect of the current reversal on the formation of the white coating and, in turn, on the performance of the electro-oxidation process. Since the loss of electrons and release of ferrous ions take place at the anode, it was expected that the periodic conversion of the cathode into anode would result in the removal of precipitated salt on the cathode. The experiments were conducted at optimum conditions of current density and contact time (30 mA cm^{-2} and 5, 10, 20, and 30 min). It is worth to mention that no kaolin was used in these experiments and the reversal of current direction was conducted every 4 min, for all experiments.

Fig. 7 shows the effect of current density on the degradation of phenol at different contact times, when current was reversed every 4 min. Comparing the figure with the results obtained in Fig. 6 (no current reversal was applied), it is clear that the difference in phenol degradation is insignificant. Samples collected after 10 min of experiment periods revealed that phenol concentrations were 20, 28, 0, and 26 mg/L for contact times of 5, 10, 20, and 30 min (Fig. 7), respectively. Without applying current reversal, the concentrations of phenol were 15, 32, 2, and 22 mg/L under similar operating conditions (Fig. 6). It is important to

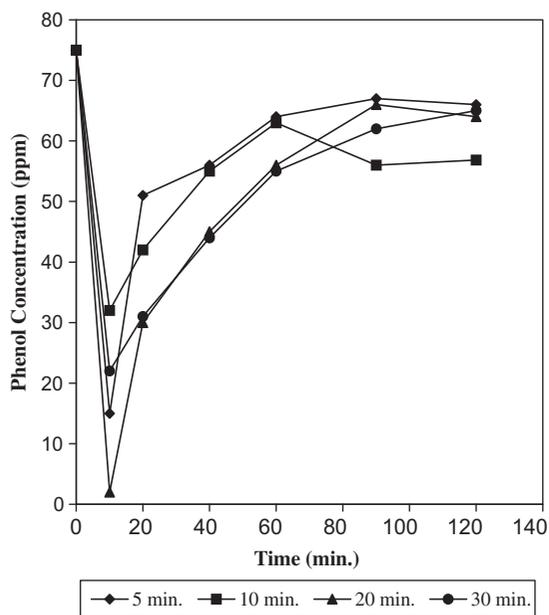


Fig. 6. Phenol concentration after electrochemical treatment without kaolin in wastewater.

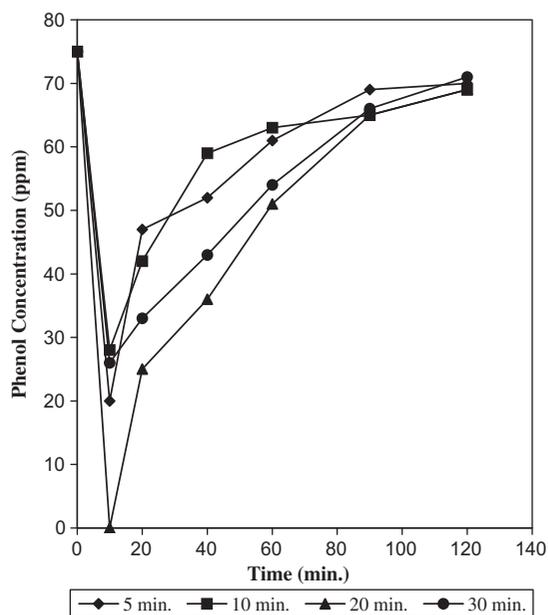


Fig. 7. Phenol concentration after electrochemical treatment with periodic reversal in current direction.

mention here that no formation of the white coating was observed at the end of the experiment.

The results in Fig. 7 clearly demonstrate that the white coating had no effect on the degradation of phenol. Phenol electropolymerization occurring on a passivated surface of stainless steel electrodes in carbonate aqueous medium resulting in adherent and polymeric film has been also been observed [67]. The characterization of tap water (TDS=1,200 mg/L) used in the preparation of the synthetic wastewater suggests the presence of carbonates in raw water. Therefore, the research was further extended to investigate the effect of using the tap water on the process performance. To carry out the investigation, deionized water with 4,000 mg/L NaCl (electrolyte) was used for the preparation of the synthetic wastewater. In this case, only one experiment was conducted at a current density of 30 mA cm^{-2} and a contact time of 20 min. It is worth to mention that the experiment was repeated 3 times, and the results reported in Fig. 8 represent average values obtained during the experiments.

A change in the removal pattern of phenol was observed as shown in Fig. 8. A complete removal of phenol was noted through UV spectrophotometric analysis after 2 min of experimental run and continued throughout the experimental period (60 min.). Also, no coating was observed to form on the cathode while the current flowed in the same direction throughout the experiment. Successful degradation of aqueous phenol waste under basic conditions (pH=12) using stainless steel electrodes has been reported [68]. The results of this experiment strongly suggest that the TDS present in raw water were the

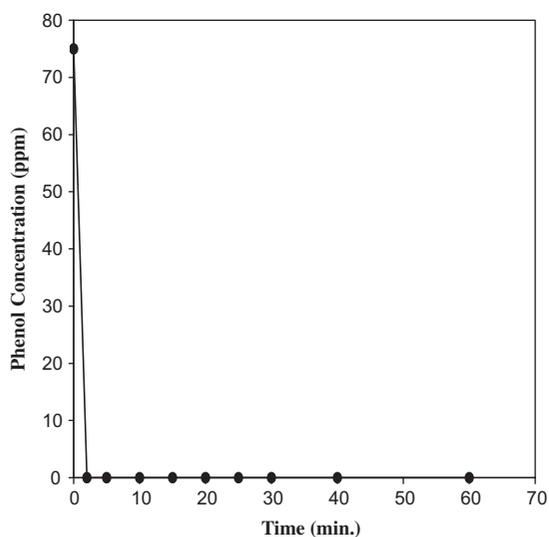
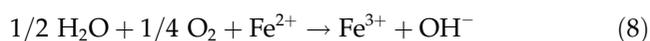


Fig. 8. Phenol concentration after electrochemical treatment with deionized water as base solvent.

main cause of interferences in the redox reactions occurring in the electrochemical cell.

Effluent samples after electrocoagulation and ultrafiltration were collected and analyzed for turbidity and oil and grease to obtain a removal profile at different operating parameters. The turbidity and oil and grease content of the synthetic wastewater were 100 NTU and 10 mg/L, respectively, for all experiments. The pattern of turbidity removal recorded after electrocoagulation and ultrafiltration treatment at a current density of 5, 15, 30, and 50 mA cm^{-2} and different contact times are shown in Figs. 9–12, respectively. These figures clearly indicate a removal efficiency of 98–99% for all the samples. Such high removal of turbidity was achieved, because the pH of zero point of charge (pH_{ZPC}) for kaolin is 3.3–4.6, making it anionic at higher pH conditions that are achieved under the performed experiments. The use of stainless steel electrodes produced iron hydroxides as shown in the following equations:

Anode reaction



Cathode reaction



The applied current facilitated the OH^- ion migration to the anode. This resulted in high pH near the

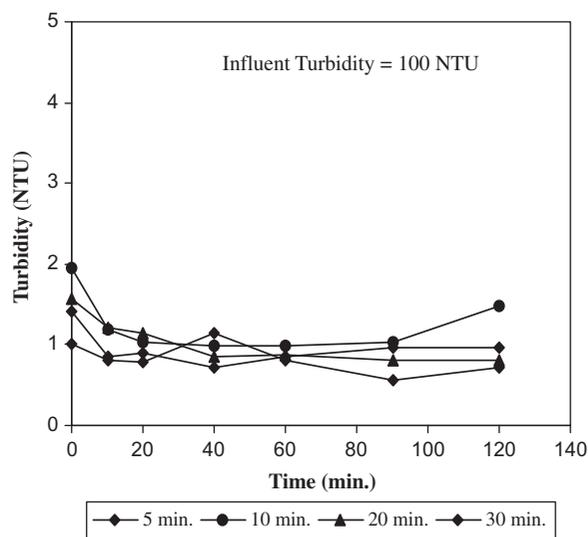


Fig. 9. Turbidity in final effluent at 5 mA cm^{-2} and different contact times.

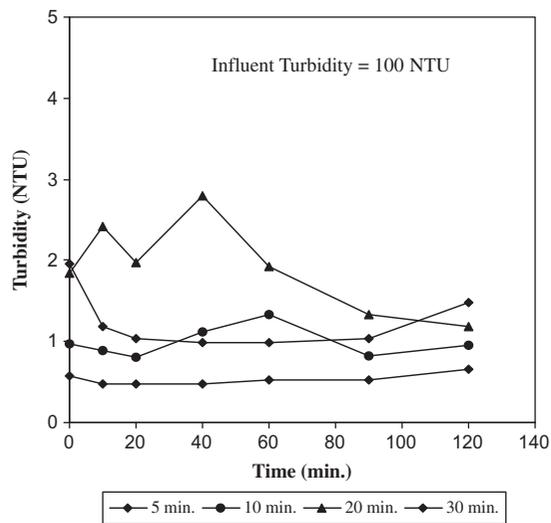


Fig. 10. Turbidity in final effluent at 15 mA cm^{-2} and different contact times.

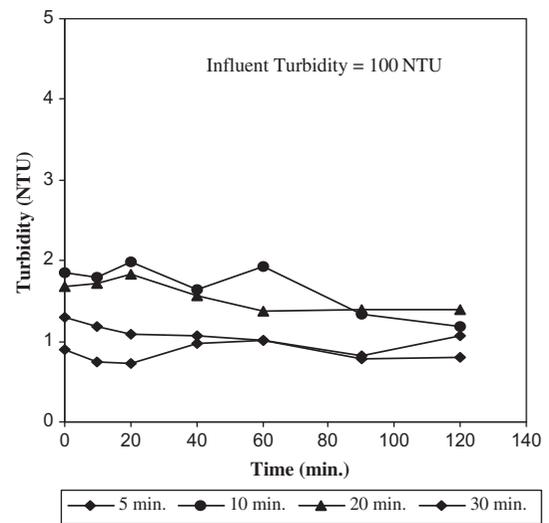


Fig. 12. Turbidity in final effluent at 50 mA cm^{-2} and different contact times.

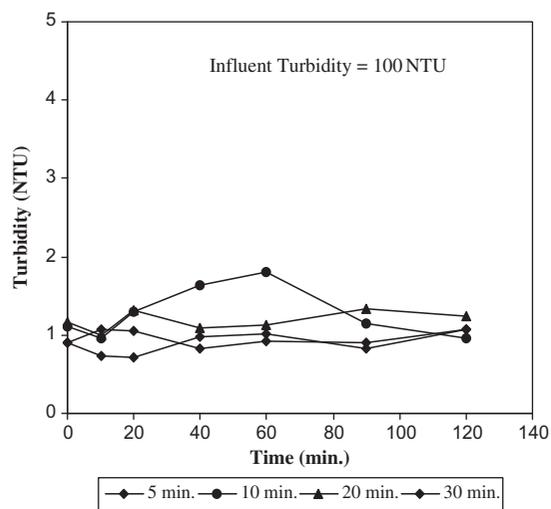


Fig. 11. Turbidity in final effluent at 30 mA cm^{-2} and different contact times.

anode that favored the formation of ferric hydroxide $[\text{Fe}(\text{OH})_3]$. Kaolin particles may have provided condensation sites, where the precipitates could have formed, and hence, the colloids were entrapped in the ferric hydroxide precipitates [69]. The water is then filtered through ultrafiltration membrane to remove the iron hydroxide precipitates with entrapped kaolin particles.

With respect to oil and grease, the EPA method 1664 (N-hexane extractable material and silica gel-treated N-hexane extractable material by extraction and gravimetry) was used to measure the concentration of oil and grease in the collected effluent samples. The minimum detection limit (MDL) of this analytical

method was reported to be 1.4 mg/L . As shown in Table 3, most of the samples analyzed through this method yielded a value that is below the MDL. Though these results cannot be reported as exact concentrations due to the fact that they are below the MDL, however, it may be deduced that the concentrations were lower than 1.4 mg/L in the collected samples, which suggests a removal efficiency of more than 86 percent.

The breaking of oil emulsion and formation of larger oil droplets through electrocoagulation is an established process. It is now used for many commercial applications. The electroacoustic measurements show that the oil emulsion droplets carry a substantial surface charge that can be calculated using Shilov's theory for overlapped diffuse layers [70]. The application of electric current on stainless steel electrodes induces dissolution of iron and formation of polymeric hydroxide species. Charge neutralization and coalescence of droplets is initiated in the electrochemical cell and continued during transfer of the aqueous

Table 3
Oil concentration in final effluent

Current density (mA/cm^2)	Contact time (min)	Oil in final effluent (mg/L)
15	10	1.7
15	20	0.9*
30	20	1.1*
50	10	0.55*
50	20	1.5

Note: *Value below MDL of EPA method 1664.

medium from the electrochemical cell to the ultrafiltration chamber. The immersed membrane retained the coalesced droplets effectively.

4. Conclusions and recommendations

The use of a continuous electro-oxidation process in treating synthetic petroleum wastewater was investigated. It was found to be effective for the removal of colloidal particles that cause turbidity. The process was also found to remove emulsified oil from wastewater successfully. Results of the investigation showed that the degradation of phenol was affected by the presence of some chemical species in the wastewater. Consequently, a thorough characterization of the raw water used for such type of studies, along with the possible reactions of different chemical species with the ions produced during electrolysis process requires detailed investigation. The main purpose of the recommended investigation is to identify species that could hinder the performance of electroredox process for the degradation of phenol. The mechanism for the complete degradation of phenol observed in deionized water is recommended to be a subject for further research. Characteristics of sludge produced at different current densities and their effect on the performance of the ultrafiltration membrane is another recommended area of investigation.

Acknowledgment

The authors would like to acknowledge the financial and technical supports provided by King Fahd University of Petroleum and Minerals, Saudi Arabia to conduct the research.

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