Removal of TOC from oily wastewater by electrocoagulation technology

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Abstract
The present study aims to employ an electrocoagulation reactor containing concentric-aluminum-tubes as electrodes for total organic carbon (TOC) removal from real oily wastewater released from drilling sites located in West Qurna-Iraq. Applied current ranges from 0.5 to 2.0 Amps and contact time ranges from 10 to 40 min had selected as the operational variables. Response surface methodology (RSM) type central composite design (CCD) and MINITAB-statistical soft program had performed to design experiments and analysis of the obtained results. The results showed significant removal of TOC (83.91%) at the optimal values of the operational parameters (1.606 Amps and 40 min). Moreover, the present design of the electrocoagulation reactor was more reliable and cost-effective that could be used in practice efficiently.

Keywords: Real oily wastewater; TOC; Electrocoagulation reactor; RSM-CCD; Optimization.

1. Introduction:

Drilling sites discharge every year huge amounts of oily wastewater containing numerous types of pollutants such as phenols, oil content, nitrate, biological oxygen demand (BOD), total organic carbon (TOC), etc. The amounts of oily wastewater may reach 15% of the produced crude oil from each site that will extremely affect the environment and caused risk for humanity [1-4].

Accordingly, researchers and scientists tried to develop many of the conventional treatment methods to overcome the threat of pollution caused by real oily wastewater, whether that occurred as a result of drilling crude oil wells or that discharged from different industrial activities such as petroleum and petrochemical factories. Adsorption, ion exchange, wetland and chemical coagulation are such examples of the conventional treatment methods which are depending, in their mechanism, on the chemical and/or physical attraction forces to eliminate different contaminants from wastewater, but they
have some disadvantages such as cost, size and continuous maintenance [5-7]. The electrochemical technique is one of the conventional treatment methods which categorized into several technologies such as electrocoagulation, electro-Oxidation, electro-Fenton, electro-reduction, etc. This technique has more attention of researchers in the last two decades due to its feasibility, treatability, simple and cost-effective [6-14].

Electrocoagulation technology is widely employed to remove different kinds of organic and inorganic pollutants from several types of wastewaters [15-22]. Practically, This method depends on several parameters; such as the type of applied current DC or AC, design of electrodes and their arrangement, type of electrodes metal and their shape, connection mode of these electrodes to the power supply, type of electrolyte, mode of operation whether batch or continuous, etc. [23-28]. The mechanism of the electrocoagulation method depends on the release of different ions from both electrodes by the dissolution process then, in consequence, these ions will interact to produce electro-coagulants, i.e. adsorbents, such as Al(OH)₃ for aluminum electrodes, to remove pollutants by adsorption process. The lightweight compounds will separate to the surface of the solution by flotation process while the heavy-weight compounds will sediment towards the base of the reactor [2,4, 29-31] as explained in Fig. 1.

Fig. 1. Schematic of electrocoagulation process

The object of this work is to remove TOC from real oily wastewater discharged from drilling sites located in Basra-south of Iraq by using an electrocoagulation reactor invented by the author in previous work [8] and optimizing the obtained results.

2. Experimental work

2.1. Chemicals and analytical

Table 1 shows the characterization of real oily wastewater treated in this study that collected from West-Qurna crude oil sites-south of Iraq. All experiments had carried out using a batch electrocoagulation reactor (Fig. 2) involves three aluminum tubes arranged
concentrically to be electrodes where the cathode electrode placed in between the two other tubes of the anode electrode, hence the total active area is 280 cm². Then, these electrodes had connected to the DC-power supply (SYADGONG company; model 305D-China; 0-5 Amps; 0-30 volt) in a parallel-monopolar mode. A magnetic agitator type ALFA company (0-1000 rpm) had used to provide 200 rpm of agitation speed for all experiments. At the end of each experiment, the analytical measurement of TOC pollutants had carried out according to the standard methods. The removal efficiency of the TOC response was estimated as revealed in Eq. 1:

\[ Y_{TOC} \% = \left( \frac{C_0 - C}{C_0} \right) \times 100 \]  

(1)

Where \( C_0 \) and \( C \) are the initial and final concentration of TOC (mg/L).

### Table 1 Properties of real oily wastewater studied in this work

| Parameters       | TOC (mg/L) | pH | Conductivity (μs/cm) |
|------------------|------------|----|----------------------|
| Value            | 34023      | 6.5| 126000               |

![Fig. 2. Schematic of the electrocoagulation reactor](image)

**2.2. Experimental design**

The present work performed response surface methodology (RSM) type central composite design (CCD) technique and Minitab-statistical program to obtain TOC removal response and analyzing the obtained findings then conducting a second-order mathematical correlation relates the studied response to the operational parameters as shown in Eq. 2 where the coefficient of variance (\( R^2 \)) is the quality indicator of this equation.

\[ Y = B_0 + \sum_{i=1}^{q} B_i X_i + \sum_{i=1}^{q} B_{ii} X_i^2 + \sum_{i=1}^{q-1} \sum_{j=i+1}^{q} B_{ij} X_i X_j + \epsilon \]  

(2)

Where: \( Y \) is the studied response of TOC removal; \( X_1, X_2, \) to \( X_q \) are the operational variables; \( B_0, B_i, B_{ii} \) and \( B_{ij} \) are the constant, linear, squared and the cross-product regression coefficients; \( \epsilon \) is the random error.
The electric current and the contact time are the most crucial variables that affect the performance of this type of wastewater treatment method; therefore, they had selected to be studied belong to the ranges shown in Table 2.

Table 2 Ranges of the operational variables

| Variables          | Ranges   |
|--------------------|----------|
| X₁: Applied current (Amps) | 0.5-2.0 |
| X₂: Contact time (min)     | 10-40    |

According to the experimental design, 11 runs required to study the present response of TOC removal under the impact of the selected operational variables.

The treatment process inside the electrocoagulation reactor is extremely dependent on the electro-coagulants generated as a result of the continuous passing of electric current throughout the electrodes; thereby, the amount of the theoretical consumption of electrodes metals accounted by using Faraday's law (Eq. 3) [4]:

\[ m_{\text{theo}} (g) = I \cdot t \cdot M / Z \cdot F \]  

(3)

Where (I) is the applied current is assigned in (Amps.), (t) is the contact time in (second), (M) is the molecular weight of electrodes metal in (g/mol.), (Z) is the number of electrons presented in the reaction (for Al is 3), and (F) is the Faraday's constant (96485.34 Columb/mol.) [15].

The consumption of energy is an important indicator of the feasibility of each type of the electrochemical reactors; therefore, it had estimated according to the following equation (Eq. 4):

\[ E = (U \cdot I \cdot t) / (1000 \cdot V) \]  

(4)

Where (U) is the applied voltage in (volts), (I) is the applied current in (Amps.), (t) is the contact time in (h), and (V) is the volume of the polluted solution in (m³).

3. Results and discussion

Table 3 shows the results obtained of TOC removal under the influence of the operational variables.

Table 3 Results of the studied parameters

| Run | X₁: Applied Current (Amps.) | X₂: Contact time (min) | TOC removal (%) | Run | X₁: Applied Current (Amps.) | X₂: Contact time (min) | TOC removal (%) |
|-----|-----------------------------|------------------------|-----------------|-----|-----------------------------|------------------------|-----------------|
| 1   | 0.72                        | 14                     | 67.78           | 7   | 0.50                        | 25                     | 66.60           |
| 2   | 0.72                        | 36                     | 76.93           | 8   | 2.00                        | 25                     | 74.49           |
| 3   | 1.78                        | 14                     | 73.32           | 9   | 1.25                        | 25                     | 76.35           |
| 4   | 1.78                        | 36                     | 82.77           | 10  | 1.25                        | 25                     | 76.11           |
| 5   | 1.25                        | 10                     | 68.59           | 11  | 1.25                        | 25                     | 76.00           |
| 6   | 1.25                        | 40                     | 81.79           |     |                             |                        |                 |

3.1 Effect of the applied current
Electrochemical reactors are completely dependent, in their operation, on the electric current supplied to the electrodes involved [8,19]; therefore, the present work had investigated the effect of this independent parameter on the behavior of the electrocoagulation removal of TOC from wastewater. At the mean range of the contact time, Fig. 3 reveals that an increase of the applied current led to increasing the treatability of the present reactor where the TOC removal efficiency increased from 66.60% at (0.50 Amps) to 74.49% at (2.0 Amps) which means that the concentration of TOC pollutant decreased from 11362.1 to 8680.82 ppm [23]. The nearest interpretation of this behavior could be as an increase of the applied current will cause to release more of different ions from both electrodes, such as aluminum and hydroxyl ions, that required to form electro-coagulants needed for the adsorption process. Moreover, the continuous evolution of bubbles will assist the floatation process of lightweight pollutants toward the surface of the solution. The decrement of the removal efficiency, as observed in Fig. 3, was occurred due to a huge amount of mini-bubbles formed and accumulated on the surfaces of both electrodes which led to minimizing the releasing of Al-OH ions required for the generation of adsorbents then TOC removal tends to slightly minimize [11, 29, 30].

![Fig. 3. The effect of applied current on the TOC removal efficiency of 34023 mg TOC/L of real oily wastewater (contact time= 25 min)](image)

Thereby, the contact time parameter should be studied also to provide a sufficient amount of current applied to prevent any risk of economical determination.

3.2 Effect of the contact time

The contact time is a very important parameter in the electrocoagulation treatment process. This parameter controls the amount of different ions and gas bubbles released inside the reactor then, in consequence, the elimination of pollutants by the adsorption-floatation process. Therefore, the contact time of this system was chosen in the range of 10-40 min to investigate the treatability of the electrocoagulation reactor that composites of concentric electrodes. The observed results in Fig. 4 proved that the TOC removal
efficiency had increased along the treatment period when the applied current fixed at its mean value. The concentration of TOC pollutants had sharply minimized from 10685.3 ppm within 10 min to 6195.3 ppm at the ultimate range of the contact time designed which means that the maximum removal efficacy of TOC attained was 81.79% at (1.25 Amps) of the applied current [4, 24,29]. So, the optimal value of the contact time should be estimated to inform which value should be taken in practical applications.

![Fig. 4. The effect of contact time on the TOC removal efficiency of 34023 mg TOC/L of real oily wastewater (applied current= 1.25 Amps.)](image)

Eq. 5 relates the response of TOC removal to the operational variables of applied current and contact time where the values of the regression coefficient (R²), the adjusted regression coefficient (R²_adj) and the predicted regression coefficient (R²_pred) obtained were higher (96.09%, 92.17% and 72.28%) which means that the obtained model of TOC removal efficiency is desirable.

\[
Y_{TOC} \% = 17969 - 8410 X_1 - 128 X_2 + 2686 X_1^2 - 0.31 X_2^2 - 4.50 X_1 X_2 \quad (5)
\]

3.3 ANOVA analysis

To descript the estimated model, adequately, and fitting the function to the obtained data, analysis of variance (ANOVA) method was utilized. Table 4 shows the results of ANOVA test for TOC removal where if the value of Prob (P) is less than 0.05, the terms of the estimated model are significant, but it will classify as an insignificant model when its Prob (P) is larger than 0.10 value.

| Source | Degree of Freedom | Sum of squares | Mean square | F-Value | P-Value |
|--------|------------------|----------------|-------------|---------|---------|
| Model  | 5                | 31078983       | 6215797     | 24.55   | 0.002   |
|        |                   |                |             |         | (significant) |
| X₁     | 1                | 7348944        | 7348944     | 29.03   | 0.003   |
| X₂     | 1                | 20094459       | 20094459    | 79.38   | <0.001  |
| X₁²    | 1                | 3224140        | 3224140     | 12.74   | 0.016   |
| X₂²    | 1                | 6937           | 6937        | 0.03    | 0.875   |


As conducted from Table 4 that the squared term of the contact time, as well as the interaction between both variables, are insignificant (Bolded P-values) which means that applied current influenced the treatment process more than the contact time and the two terms should be omitted from the regression model to be as shown in Eq. 6, moreover, the higher value of F-indicator (24.55) indicates that the estimated model is significant.

\[ Y_{TOC} \% = 17969 - 8410 X_1 - 128 X_2 + 2686 X_1^2 \]  

(6)

3.4 Optimization of the operational variables

The optimal values of the operational parameters, applied current and contact time, were evaluated as 1.606 Amps and 40 min, respectively, using the statistical Minitab program which hence the composite desirability (D-indicator) of these results equals 1. The values of TOC removal efficiency and its concentration at the optimal values of the studied variables were 83.91% and 5475.57 mg TOC/L as shown in Fig. 5 [23,25].

![Fig. 5. The optimum values of the studied variables for the treatment of 34023 mg TOC/L of real oily wastewater](image)

As revealed in Fig. 5, the applied current is the dominant variable and it controls the treatment process of TOC removal from real oily wastewater [23]. Accordingly, the values of consumption of energy and electrodes at the optimal values of the applied current and contact time were determined as 4.447 kWh/m³ and 0.40 g, respectively, which proved that
present electrocoagulation reactor is cost-effective [32] and can treat real wastewater containing total organic carbon (TOC) with a higher value of removal efficiency.

4. Conclusion

The present work focuses on an essential threat caused by oily wastewater pollution that, always, impacts the environment. A batch electrocoagulation reactor containing triple concentric electrodes with a parallel-monopolar arrangement mode is employed to increase the treatability of the conventional electrocoagulation reactors under the influence of the operational variables selected which are the applied current and the contact time. Higher removal efficiency (83.91%) of total organic carbon (TOC) obtained at the optimal values of the operational parameters (1.606 Amps and 40 min). The observed results at the optimal values revealed that the present design of the electrocoagulation reactor is cost-effective and economic.

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