Performance of Combined Electrocoagulation-Advanced Electrochemical Oxidation Used for Oil Field Produced Water Treatment

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Abstract

Considerable amounts of produced water (PW) are usually accompanied with the production of oil. This study proposed a combination of electrocoagulation (EC) - electro-Fenton (EF) process for oxidation organic compounds in PW to reduce the chemical oxygen demand (COD) to below regulation limits. The PW used in this study was collected from oilfield in the Midland Oil Company. Pretreatment of the PW was conducted using batch EC technique with aluminum electrodes to eliminate the suspended and dissolved solids and to reduce the COD and treatment cost. Optimization of EC process revealed that optimum current density, pH, and reaction time were 7.83 mA/cm2, 7.24, 20.40 minutes respectively. Under these conditions the COD removal percentage was 73.97% starting from initial COD of 1730 mg/l. Batch and continuous electro-Fenton processes were investigated using dimensionally stable anode Ti-RuO2/IrO2 and activated carbon fiber felt (ACFF) cathode. The effect of crucial process variables on COD removal efficiency was investigated using response surface methodology. A second order polynomial model equations were constructed and the results was analyzed by the analysis of variance (ANOVA). It was concluded that a combination of electrocoagulation followed by electro-Fenton process is effective for treating oilfield produced water and further improvement can be achieved by photo assisting the process. A total COR removal efficiency of 98% was achieved.

Keywords: Electro-Fenton; Produced water; Response surface methodology; COD removal.
1. Introduction

Oil is produced with large volume of wastewater that is estimated three barrels of water produced for every barrel of crude oil [1]. A number of countries have implemented stricter regulations for discharging PW [2]. Produced water (PW) is a complex mixture of dissolved and particulate organic and inorganic chemicals in water (mostly oils, salts, and minerals) [3]. Some factors such as geological location of the field, lifetime of its reservoirs affect the physical and chemical properties of produced water.

The oil content in produced water is frequently classified into four groups according to its nature of physical phase, which are: free oil (larger than 150 µm), dispersed oil (20-150 µm), emulsified oil (less than 20 µm), and dissolved oil. Treatment methods of produced water can be classified into three main categories namely, primary to separate free oil (larger than 150 µm) such as gravity separators, secondary to removal dispersed oil (20-150 µm) such as coagulation and flotation processes, and tertiary treatment to eliminate emulsified (less than 20 µm) and soluble oil such as advanced oxidation processes (AOPs).

Electrochemical technology has been widely applied in treatment of different types of wastewater, but it is rarely used in the treatment of produced water. Progress in research and electrochemistry knowledge encourages the use of electrochemical methods in produced water. Electrochemical approach is a green technology and it is relatively cheap. It does not involve the use of additional chemicals nor generate secondary waste, and offers more favourable uses of produced water. It eliminates organic pollutants, recover valuable substances, and produce clean water with no negative influence on the environment [18].

Electrocoagulation (EC) is an electrochemical technique where coagulants are in-situ generated by passing direct current through the cell. Sacrificial anodes (mostly aluminium and iron) are dissolved to generate the coagulants. Hydrogen gas is evolved at the cathode and oxygen gas may be evolve at the anode. Hydrogen bubbles adsorb the flocs formed by the process, and ensure their flotation. Electrocoagulation is hybridization of electrochemistry, coagulation and flotation.

The results on the investigation of the electrocoagulation process for treating oily wastewater showed that using electrocoagulation destabilize successfully oil-in water emulsions [19]. Although it needs more studies for improving the conditions and removal efficiency of COD [1]. For some cases, it is necessary to use further treatment such as electro-
oxidation (EO) when EC is not capable to reduce COD with respect to the regulation limits [20]. New AOPs based on the electrochemical technology have been investigated in recent years, i.e., the so-called Electrochemical Advanced Oxidation Processes (EAOPs) have been developed. The EAOPs provides several advantages for the prevention and remediation of pollution problems because electron is a clean reagent. Other advantages include high energy efficiency, amenability to automation, easy handling because of the simple equipment required and safety because they operate under mild conditions (room temperature and pressure) [4].

The conventional Fenton method achieved by the addition of Fe (II) salt to hydrogen peroxide (H$_2$O$_2$) in aqueous media has been found since the end of the 19th century. This Fenton reaction generates hydroxyl radicals (•OH) under acidic conditions that can oxidize organics and convert it to non-toxic products. However, this Fenton process produces large amounts of Fe(III) oxyhydroxide solid byproduct that inhibiting the catalytic role of Fe(II) in generating •OH [5]. Electro-Fenton (EF) is one approach to resolve this issues in conventional Fenton. In EF the Fe(III) reduced to Fe(II) at the cathode. Also, hydrogen peroxide in-situ generated at the cathode [5].

In the EF process, hydroxyl radicals are produced by the reaction between hydrogen peroxide and ferrous ions, which can destroy organic compounds. The reduction of ferric ion to ferrous ion, which can reduce iron sludge production is one advantage of the EF process over the conventional Fenton process [6].

Electro-Fenton mainly relies on in situ and catalytic electro generation of Fenton’s reagent – a mixture of Fe(II) ions and hydrogen peroxide (H$_2$O$_2$) to produce hydroxyl radicals (•OH) and react with organic pollutants in aqueous media, leading to their destruction (as equations 1-4) [7].

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{Fe}^{2+} &\rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot\text{OH} \\
\text{RH} + \cdot\text{OH} &\rightarrow \text{R}\cdot + \text{H}_2\text{O} \\
\text{R}\cdot + \text{O}_2 &\rightarrow \text{products} \\
\text{R}\cdot + \cdot\text{OH} &\rightarrow \text{products}
\end{align*}
\]

The optimum pH for COD removal is 3. A pH greater than 3 lower the COD removal efficiency. At a higher pH, the oxidation efficiency of EF process decreases due to the formation of low active Fe(OH)$_3$, which has a lower tendency to react with hydrogen peroxide
[6]. pH lower than optimum affects the pollutant removal by producing less hydroxyl radicals, increased scavenging effects of $\text{H}^+$ and hydroxyl radicals [8].

Electro-Fenton method has been applied successfully for the treatment of various wastewater such as paper mill wastewater [9], fertilizer manufacturing wastewater [10], Diary industry wastewater [11], synthetic dye wastewater [12], photographic processing wastewater [13], and petroleum refinery wastewater [14].

The traditional technique of experimental design, in which one process variable is changed while the other variables are settled, does not demonstrate the interaction between the process variables. Response surface methodology (RSM) is able to assess this interaction [6]. Response surface methodology finds the optimum values of process variables for a desirable response by using a statistical-based technique to evaluate the simultaneous effects between these variables [16] and [17].

The main aim of this study is to investigate the performance of electrochemical advanced oxidation process (EAOP) combined with electrocoagulation for the elimination of organic pollutants from industrial wastewater.

2. Material and Methods

2.1. Produced water sample

The produced water sample was collected from oilfield, midland oil company, Iraq. The properties of the produced water are summarized in Table (1).

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Value</th>
<th>Characteristics</th>
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<th>Characteristics</th>
<th>Value</th>
<th>Characteristics</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH (-)</td>
<td>6.5</td>
<td>Chloride (mg/l)</td>
<td>101898</td>
<td>Oil and greases (mg/l)</td>
<td>654</td>
<td>Sodium (mg/l)</td>
<td>47981</td>
</tr>
<tr>
<td>Density (kg/m$^3$)</td>
<td>1150</td>
<td>Calcium (mg/l)</td>
<td>10926</td>
<td>TSS (mg/l)</td>
<td>290</td>
<td>HCO3 (mg/l)</td>
<td>567</td>
</tr>
<tr>
<td>Conductivity (mS/cm)</td>
<td>210</td>
<td>Magnesium (mg/l)</td>
<td>3251</td>
<td>TDS (mg/l)</td>
<td>165950</td>
<td>Turbidity (NTU)</td>
<td>211</td>
</tr>
<tr>
<td>COD (mg/l)</td>
<td>1730</td>
<td>Sulfate (mg/l)</td>
<td>773</td>
<td>Oil and greases (mg/l)</td>
<td>654</td>
<td>Sodium (mg/l)</td>
<td>47981</td>
</tr>
</tbody>
</table>

It can be noticed that PW sample have a very high salinity, dissolved solids, turbidity and chlorides. It contains high concentrations of organic pollutants, COD, oil and grease. These pollutants may cause serious threat to the environment if disposed without proper treatment.
2.2 Experimental System Description:

2.2.1 Electrocoagulation Experimental System

Electrocoagulation was conducted at room temperature (25 ± 2 °C) in a cylindrical glass reactor with a working volume of 1000 ml and the solution was rigorously stirred with a magnetic stirrer (Jenway1000, UK) at 500 rpm. The electrodes used were two aluminum plates (purity > 99%), one serving as a cathode and the other as anode, with an effective surface area of 40 cm² each. The inter-electrode distance was 2 cm. A laboratory model DC power supply (Yaogong 1052DD, China) was used to maintain constant DC current and to measure voltage and current. A schematic diagram and photograph of the apparatus are shown in Figures (1) and (2). The most used material as sacrificial anodes are aluminum and iron because they are cheap, readily available and proven effective. The formation of Fe(OH)₃ as result of the reaction of Fe³⁺ with OH⁻ ions gives yellow color to the water and increase turbidity. This phenomenon a reason for choosing aluminum electrodes for electrocoagulation processes [21].

![Fig. (1) Schematic diagram of electrocoagulation experimental system.](image1)
(1) DC power supply; (2) EC cell; (3) Teflon bar (4) Magnetic stirrer

![Fig. (2) Photograph of the electrocoagulation experimental system.](image2)
2.2.2 Batch Electro-Fenton experimental System

Treatment of PW by the electro-Fenton process was performed at the room temperature (25±2 °C) in a cylindrical glass electrochemical cell of 1 L equipped with two electrodes. The cathode was a cylindrical activated carbon fiber felt (ACFF) (33×8 cm). The anode was Ti-RuO₂/IrO₂ mesh (8×3 cm) placed in the center of the cell. The solution was rigorously stirred with a magnetic stirrer (Jenway1000, UK) at 500 rpm to keep the homogeneity of the electrolyte concentration. A laboratory model DC power supply (Yaogong 1052DD, China) was used to maintain constant DC current and to measure voltage and current. Compressed air was fed to the cathode by an air pump with 2.5 L/min for 15 min before the power was on and was maintained during the process of electrolysis. The pH was measured by pH-meter (Hanna Instruments pH 211) calibrated with a standard buffer at pH values of 4.0 and 7.0. Initial pH of solution was adjusted to three by diluted H₂SO₄ solution (0.1M) and remained almost constant. This pH was chosen in order to optimize the production of hydroxyl and to avoid the formation of peroxyo and sulphate complex. Figure (3) shows the schematic diagram of the experimental work. Figure (4) is a photograph of the experimental system used in this work.

![Fig. (3) Schematic diagram of batch electro-Fenton experimental system.](image1)

![Fig. (4) Photograph of batch electro-Fenton experimental system.](image2)

2.3. Analytical procedure

All samples were filtered through Whatman filter paper with a pore size of 11 µm. COD was analyzed using a COD thermoreactor (RD125, Lovibond) and a direct reading spectrophotometer (MD200, Lovibond), whereas, the equation used to calculate the percentage of COD removal (R%) is shown below:

\[ R\% = \frac{COD_o-COD}{COD_o} \times 100 \] (10)

Where COD₀ and COD are the initial and final chemical oxygen demand respectively.
2.4. Experimental Design

A total of 20 experiments were performed to optimize and determine the relationship between the removal efficiency of COD and energy consumption with respect to crucial operating parameters, i.e., current density 5-15 mA/cm², initial pH 7-11 and treatment time 5-30 min. Response surface Methodology (RSM), the central composite design (CCD) was performed using MINITAB software (version 17). Experimental data were fitted to a second-order polynomial model.

For electro-Fenton experiments total of 20 experiments were performed to optimize and determine the relationship between the removal efficiency of COD with respect to crucial operating parameters, i.e., initial Fe(II) ions concentration (0.1-0.5 mM), current intensity (100-500 mA), and reaction time (30-90 minutes). Response surface Methodology (RSM), the central composite design (CCD) was performed using MINITAB software (version 17). Experimental data were fitted to a quadratic equation:

\[ Y_i = b_0 + \sum b_i x_i + \sum b_{ij} x_i^2 + \sum b_{ij} x_i x_j \]  

(11)

Where \( b_0 \), \( b_i \), and \( b_{ij} \) are the regression coefficients for the equation terms. \( Y_i \) is the percentage removal of COD (R%), and electrical energy consumption (EEC). The regression coefficients were analyzed by the F-test and P-value. The statistical significance of the model was tested by the analysis of the variance (ANOVA). The relationship between the response and the variables was used to construct a three dimensional surface plots to study the effect of variables on the response. Multiple response optimization of the EC & EF processes was done to determine the optimum parameters for maximum COD removal efficiency and for minimum power consumptions.

2.5. Experimental Procedure

All electrocoagulation experiments were conducted in a batch mode under galvanostatic conditions. Before starting-up the process, the electrodes were cleaned with 1 M HCl and rinsed with deionized water to eliminate impurities from the surface of the electrodes. In each run, 800 ml of produced water was placed into the reactor and all runs were performed under stirring at 500 rpm. Initial pH values were adjusted with 0.1 M solutions of H₂SO₄ and NaOH as required.

After electrocoagulation experiments electro-Fenton experiments were conducted in a batch mode under galvanostatic conditions. Before starting-up the process, compressed air was fed to
the cathode by an air pump with 2.5 L/min for 15 minutes to saturate the solution with oxygen and was maintained during the process of electrolysis. In each run, 800 ml of produced water was placed into the reactor and all runs were performed under stirring at 500 rpm. Initial pH values were adjusted to 3 with 0.1 M solution of H₂SO₄. The average of voltage from the start to the end of experiment was used for the determination of energy consumption. One of most important parameters that affect the application of any method of wastewater treatment is the cost. The operation cost in the process includes material, consuming of energy cost, labor, maintenance, and disposal and fixed cost. Consuming of energy cost is the major cost in EF process. The electrical energy consumption (EEC) for EF treatment was calculated using the following equation [15]:

$$EEC = \frac{U \times I \times 1000}{(COD_o - COD)V}$$

(12)

where: EEC = electrical energy consumed (kWh/kg COD), U= voltage (volt), I= current intensity (A), t= time (h), V= water volume (Liter), COD₀ and COD= initial and final COD (mg/l)

3. Results and Discussion
3.1. Experimental Design Analysis for electrocoagulation process

Figs. 5-7 represent the three-dimensional (3D) response surface and two-dimensional (2D) contour plots of COD removal efficiency as a function of applied current density, pH, and reaction time.

![Contour plots](image)

Fig. (5) Surface plot and contour plot for COD removal efficiency (R%) vs pH, i, at time= 17.5 minutes.
Fig. (6). Surface plot and contour plot for COD removal efficiency (R%) vs time, i, at pH = 8.

Fig. (7) Surface plot and contour plot for COD removal efficiency (R%), vs time, pH at i=10 mA/cm².

It was found that the removal efficiency of COD increased rapidly with current density up to 10 mA/cm². It was found out that increasing current density will increase the coagulant and increase the metal hydroxide flocks and hence improve the COD removal. However, above 10 mA/cm², the current density had almost negligible effect on the COD removal efficiency. This may be attributed to the formation of a passive oxide film on the aluminium electrodes, which inhibit the electrocoagulation process. In addition, at higher current, mass transfer could be hindered by the increased gas production. Similar observation was obtained by [22, 23]. It has been established that initial pH is an important parameter influencing the performance of electrocoagulation process. From the results, it is observed that COD removal efficiency increased with increasing initial pH from 5 to 7.7. This mainly due to the formation of amorphous aluminium hydroxide with large surface area which are beneficial for the removal of COD. Beyond pH 7.7, lower COD removal efficiency was noticed which may be due to the precipitation mechanism. Similar observation was obtained by [16]. The COD removal efficiency increase with increasing reaction time up to 20 minutes. This is due to the increase in the quantity of aluminum released in the solution, which enhance the formation of aluminum hydroxide and lead to higher COD removal. Thereafter 20 minutes, the
reaction time had slight effect on the removal of COD. This can be explained by the fact that after 20 minutes most pollutants are removed as flocks. In addition, aluminium hydroxide species formed during EC stick with the electrode surface and grow like a film with time. Therefore, the removal efficiency affected due to extra resistance imposed by this film. As mentioned also by [24]. Validation experiment have been conducted at optimum operating conditions that revealed by multiple response optimization and the results are shown in Table (2). It was noticed that treating produced water by electrocoagulation totally eliminate suspended solids and turbidity and the effluent was a very clear and transparent water. The oil and grease content have been efficiently reduced from 654 to 84 mg/l. Also, the COD concentration was reduced from 1730 to 445 mg/l, COD removal efficiency of 74.25%, which in agreement with the predicted value. The effluent still has a high COD content, 445 mg/l, and needs further treatment to reduce it to below regulation limits.

Table (2) Properties of treated produced water by EC at optimum operating conditions (i= 7.83 mA/cm², pH= 7.24, and t= 20.40 minutes).

<table>
<thead>
<tr>
<th>Property</th>
<th>Before Treatment</th>
<th>After Treatment</th>
<th>Property</th>
<th>Before Treatment</th>
<th>After Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD content (mg/L)</td>
<td>1730</td>
<td>445</td>
<td>pH</td>
<td>6.5</td>
<td>7.2</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>211</td>
<td>1.7</td>
<td>COD removal efficiency (%)</td>
<td></td>
<td>74.25</td>
</tr>
<tr>
<td>Oil and Grease (mg/L)</td>
<td>654</td>
<td>84</td>
<td>Electrical energy consumption (kWh/kg COD)</td>
<td></td>
<td>0.1230</td>
</tr>
</tbody>
</table>

3.2. Experimental Design Analysis for electro-Fenton process

Three factors at three levels CCD were used in this study to investigate the effect of process variables COD removal efficiency. Figures (8-10) represents three-dimensional (3D) response surface and two-dimensional (2D) contour plots of COD removal efficiency as a function of, initial Fe(II) ions concentration (C), current intensity (I), and reaction time (t). It was found that the removal efficiency of COD increased rapidly with current intensity up to 300 mA. This can be explained to the fact that the Hydroxyl free radical formation rate is controlled by the applied I, and hence increasing I improve the COD removal. However, above 300 mA, lower COD removal efficiency was noticed which might be attributed to the increase of the ratio of (mol H₂O₂/mol Fe²⁺) above the optimum value which increase the reaction that scavenged
Hydroxyl radical leading to decrease the COD removal efficiency. It has been found that initial Fe$^{3+}$ concentration is an important parameter affecting the performance of EF process. It was observed that COD removal efficiency increased with increasing initial Fe$^{2+}$ concentration from 0.1 to 0.32 mM. This increase because of the increase of the reactive material in the reaction media due to the catalytic effect of Fe$^{2+}$. Beyond 0.32 mM lower COD removal efficiency was noticed which might be due the increase of Fe$^{3+}$ concentration which lead to the formation of yellow precipitate of Fe(OH)$_3$ which deposited on the electrode surface. The COD removal efficiency increase rapidly with increasing reaction time up to 60 minutes. Initial rapid degradation is largely due to the easily degradation organics leading to higher COD removal. Thereafter 60 minutes, the removal efficiency had slight effect on the removal of COD. This can be attributed to the presence of large molecular and complex compounds in oil which are difficult to oxidize with electro-Fenton. These molecules were degraded to simpler products and then further decomposed to simpler and lower molecules. The effect of these process parameters are in good agreements with results of the previous work of [9, 12, 13].

![Fig. (8) Surface plot and contour plot for COD removal efficiency (R%) vs C, I, at t = 60 minutes.](image)

![Fig. (9) Surface plot and contour plot for COD removal efficiency (R%) vs t, I, at C = 0.3 mM.](image)

![Fig. (10) Surface plot and contour plot for COD removal efficiency (R%), vs t, C at I=300 mA.](image)
Effect of Process Variables on EEC shown in Figures (11 – 13) which represents the three-dimensional (3D) response surface and two-dimensional (2D) contour plots of electrical energy consumption as a function of applied current intensity, initial Fe$^{2+}$ concentration, and reaction time. EEC values of the present study were calculated for a given amount (kg) of COD removed. From the obtained results, it was found that initial Fe$^{2+}$ concentration have insignificant effect on EEC. Meanwhile, applied current intensity has a significant effect on EEC. Also, it was found that EEC increase linearly with the time of reaction. In this study, the EEC values varied in the range of 0.2296 to 5.9974 kWh/kg COD.

Fig. (11) Surface plot and contour plot for EEC vs C, I, at t = 60 minutes.

Fig. (12) Surface plot and contour plot for EEC vs t, I, at C = 0.3 mM.

Fig. (13) Surface plot and contour plot for EEC vs t, C at I=300 mA.
3.3 Optimization and Validation

Multiple response optimization was performed for maximizing COD removal efficiency (R%) while minimizing electrical energy consumption (EEC). The optimization gave initial Fe$^{2+}$ concentration of 0.322 mM, current intensity of 249.5 mA, and reaction time of 60.91 minutes as optimal points. The optimization predicts removal efficiency of 83.42% and energy consumption of 1.163 kWh/kg COD at these optimal points. Fig. 14 illustrate the response optimization of COD removal efficiency, and electrical energy consumption.

Validation experiment conducted under the optimal parameters gave 82.88% COD removal efficiency and 1.170 kWh/kg COD electrical energy consumption, which in agreement with the predicted values.

![Fig. (14) Multiple response optimization of COD removal efficiency (R%), and electrical energy consumption (EEC).](image)

Validation experiment have been conducted at optimum operating conditions that revealed by multiple response optimization (I= 249.5 mA, C= 0.322 mM, and t= 60.9 minutes) and the results are shown in Table (3). It was noticed that electro-Fenton have been succeeded in mineralizing organic pollutants in the produced water. The COD concentration was reduced from 457 to 78 mg/l, COD removal efficiency was 82.90% which is in agreement with the predicted value. The effluent can be easily neutralizing to pH 7 by adding few drops of diluted NaOH solution. The effluent is within the allowable regulation limits of organic pollutants concentration.
### Table (3) Properties of treated produced water by batch EF at optimum operating conditions (I= 250 mA, C= 0.322 mM, and t= 60.9 minutes).

<table>
<thead>
<tr>
<th>Property</th>
<th>Before Treatment</th>
<th>After Treatment</th>
<th>Property</th>
<th>Before Treatment</th>
<th>After Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD content (mg/L)</td>
<td>457</td>
<td>78</td>
<td>pH</td>
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<td>3</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
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<td>-</td>
<td>COD removal efficiency (%)</td>
<td></td>
<td>82.90</td>
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<tr>
<td>Oil and Grease (mg/L)</td>
<td>86</td>
<td>-</td>
<td>Electrical energy consumption (kWh/kg COD)</td>
<td></td>
<td>1.170</td>
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</tbody>
</table>

### 4. Conclusions

1. Combined Electrocoagulation and Electro-Fenton process have been successfully implemented for treating of oilfield produced water using response surface methodology (RSM).

2. Pre-treatment of produced water is needed before degradation of organic pollutants by electro-Fenton. Electrocoagulation (EC) is a successful method to eliminate suspended and dissolved solids and to reduce COD and treatment cost. In this study, the turbidity was reduced from 211 to 1.7 NTU in the EC treatment.

3. For EC treatment and in the range of parameters used in this study, it was found that the COD removal efficiency (R%) increased rapidly with current density up to 10 mA/cm², above 10 mA/cm², the current density had almost negligible effect. Also, R% increase with reaction time up to 20 minutes, after that the time had slight effect.

4. Multiple response optimization for maximizing COD removal efficiency while minimizing electrical energy consumption revealed that the optimum initial Fe²⁺ concentration, current intensity, and reaction time are 0.322 mM, 249.5 mA, and 60.91 minutes respectively.
References


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