Treatment of Petroleum Refinery Wastewater by Sono Fenton Process Utilizing the in-Situ Generated Hydrogen Peroxide

Marwa M. Jiad* Ali H. Abbar**

*,**Department of Biochemical Engineering/Al-Khwarizmi College of Engineering/University of Baghdad/Baghdad/Iraq
*Email: Marwa.jeyad2205m@kecbu.uobaghdad.edu.iq
**Email: ali.abbar@kecbu.uobaghdad.edu.iq

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Abstract

Combining ultrasonic irradiation and the Fenton process as a sono-Fenton process, the chemical oxygen demand (COD) in refinery wastewater was successfully eliminated using response surface methodology (RSM) with central composite design (CCD). The impact of two main influential operational parameters (iron dosage and reaction time) on the COD removal from wastewater generated by an Iraqi petroleum refinery facility was explored. Removal of 85.81% was attained under the optimal conditions of 21 minutes and 0.289 mM of Fe²⁺ concentration. Additionally, the results revealed that the concentration of Fe²⁺ has the highest effect on the COD elimination, followed by reaction time. The high $R^2$ value (96.40%) validated the strong fit of the model equation and the successful adopting RSM in the treatment of wastewaters from petroleum refineries. Furthermore, a comparison among sono-Fenton, sono-Fenton with addition of $H_2O_2$ externally, classical Fenton and sonolysis processes showed that the combined process of sono-Fenton is better than individual processes and the external addition of $H_2O_2$.

Keywords: COD removal, Hybrid processes, Petroleum refinery wastewater, Hybrid processes, Sono-Fenton; Sonolysis, Response surface methodology.

1. Introduction

Water is vital to life because it is a necessity for all species. The rapid economic and industrial expansion has facilitated rapid population growth and development [1]. The world is experiencing industry expansion and growth using different industrial methods [2]. Continuously producing massive volumes of wastewater at high rates is an environmental issue. These are often discarded without effective management and treatment [3, 4]. From an economic growth standpoint, petroleum refineries and industries are massively important [5].

Between 2010 and 2017, OPEC liquids rose to an average of 1.9 to 1.8 mb/d, with a significant contribution from Iraq (millions of barrels daily) [6]. There are more than 15 refineries in Iraq, including the refineries in the Kurdistan province, and the refining total amounts to more than 1 million barrels per day [6]. How to dispose of this wastewater poses a challenge for petroleum refineries.

Petroleum industry wastewater comprises several organic and inorganic pollutants, sulfides, and heavy metals [7]. Petroleum industry activities, such as oil production, oil refining, transportation, and storage, generate vast quantities of environmental and human health dangerous compounds [6]. Various physical, chemical, and biological techniques were utilized to treat wastewater the petroleum sector creates [8]. However, the bulk of these techniques are not
suggested for separating the various groups of chemicals and are best suited to meet the specific treatment needs of each application [9]. Consequently, there is an immediate need to develop effective and environmentally friendly technologies for cleaning contaminated waters from petroleum refineries and decreasing or eliminating contaminants.

In the 1980s, advanced oxidation processes (AOPs) were first found for the treatment of drinking water by Glaze et al. (1987) and were later extensively studied for the treatment of various wastewaters [10]. During the AOP treatment of wastewater, adequate hydroxyl radicals (OH•) or sulfate radicals (SO₄•) are generated to remove refractory organic matters, trace organic contaminants, or certain inorganic pollutants or to increase wastewater biodegradability as a pre-treatment prior to a subsequent biological treatment [11, 12]. Multiple types of AOPs rely on the in-situ formation of OH• radicals via chemical, photo-chemical, sono-chemical, or electro-chemical reactions. Ultrasound is a superior method of AOPs, in which water molecules break up and release OH• due to high-frequency acoustic cavitation. After the generation of OH•, the hydroxyl radicals attack the organic pollutant to degrade it (Eq.1 and Eq.2) [13]. Over the last few years, ultrasound has been widely used to remove/degrade organic pollutants from water/wastewater [13].

\[
\begin{align*}
\text{H}_2\text{O}^+ & \rightarrow \text{OH} \cdot + \text{H} \cdot \\
\text{Organic pollutant} + \text{OH} \cdot & \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\end{align*}
\]

Where: \(\cdot\cdot\cdot\) denotes the ultrasound waves.

Sono-lysis creates acoustic cavitation, which involves producing and developing high-energy microbubbles when subjected to periodic pressure. When these bubbles rupture, an increase in temperature (5000 K) and pressure (500 bar) accelerates the dissociation of hazardous chemicals [14].

However, water sono-lysis has several drawbacks, including insufficient OH• production, which results in a lower degradation efficiency of organic pollutants [15]. Consequently, several studies have been conducted to combine sono-lysis with other AOPs to improve the overall efficacy of organic pollutant degradation [15-18].

The Fenton method, which uses a mixture of soluble iron (II) salt and hydrogen peroxide (Fenton’s reagent) to degrade and eliminate refractory organic contaminants, is the oldest and most common chemical AOP (Eq. 3) [19].

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH} \cdot
\]

The Fenton method is favoured among AOPs because it is user-friendly, has a short reaction time, and runs at room temperature and pressure, making it more cost-effective. In addition, it had other disadvantages, including a narrow pH range and an excessive amount of iron sludge [20]. To overcome classical Fenton’s limitations, many researchers combine the Fenton process with other AOPs, such as sono-lysis [21, 22]. It is generally known that ultrasonic irradiation of water produces hydrogen peroxide (Eq. (1) and Eq. (4)) [23, 24, 25]. However, only a few researchers depend on the amount of H₂O₂ produced by the sonication of water because it is minimal [26].

\[
2\text{OH} \cdot \rightarrow \text{H}_2\text{O}_2
\]

It is worth noting that all local works done in sono-Fenton, were done by adding H₂O₂ externally, and only a few global works were done depending on the in-situ sono-generated H₂O₂.

This study focuses on the combined application of ultrasound and the Fenton process for treating natural petroleum refinery wastewater from the Al-Diwania refinery plant located in Iraq. The effect of two crucial operating parameters (Fe dosage and reaction time) on the chemical oxygen demand (COD) removal rate was investigated by adopting response surface methodology (RSM).

2. Materials and Methods
2.1 Properties of actual refinery wastewater

In this investigation, the chosen pollutant was resistant organic COD from the Iraqi Al-Diwania refinery. Prior to the biological treatment stage, 15L of effluents were been obtained from the storage tank and refrigerated at 4°C until use. Table 1 displays the sample properties submitted by the refinery administration before treatment and after treatment.
Table 1. Properties of refinery plant wastewater

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Initial</th>
<th>Final</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.6</td>
<td>7.3</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>25</td>
<td>22</td>
<td>ºC</td>
</tr>
<tr>
<td>TDS</td>
<td>5566</td>
<td>4898</td>
<td>ppm</td>
</tr>
<tr>
<td>Phenol</td>
<td>18.5</td>
<td>0.05</td>
<td>ppm</td>
</tr>
<tr>
<td>COD</td>
<td>550</td>
<td>102</td>
<td>ppm</td>
</tr>
<tr>
<td>BOD</td>
<td>180</td>
<td>20</td>
<td>ppm</td>
</tr>
<tr>
<td>Oil</td>
<td>25.2</td>
<td>11.6</td>
<td>mg/L</td>
</tr>
<tr>
<td>Turbidity</td>
<td>33</td>
<td>7.29</td>
<td>NTU</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>0.12</td>
<td>0.8</td>
<td>Ppm</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>900</td>
<td>450</td>
<td>Ppm</td>
</tr>
</tbody>
</table>

2.2 Chemicals

Ferrous sulfate (FeSO₄·7H₂O; 99% pure) and hydrogen peroxide (H₂O₂,35%) were used as Fenton’s reagents and the pH of solution was adjusted using sulfuric acid (1M) and sodium hydroxide (1M). Potassium Permanganate (KMnO₄) employed in a titration to estimate the concentration of H₂O₂ produced in situ. All substances were diluted with deionized water to reach the desired concentrations and the used chemicals were purchased from Sigma-Aldrich Co. (Japan).

2.3 Sono-Fenton system and procedure

Ultrasonic bath from (ISOLAB Laborgerger GmbH, Germany) was used for ultrasound irradiation. In which constant ultrasonic power was obtained (60 W) and constant frequency (40 KHz). Before start any experiment, the ultrasonic bath was switch on and setting the temperature on 25 ºC for a period of 15min. A 250 ml of wastewater was put in 500 ml conical flask the pH was adjusted to 3 using 1M H₂SO₄, and the suitable amount of ferrous sulfate was added. After that, the conical flask was closed from top by rubber stopper and placed inside the ultrasonic bath. The flask was fixed by a stand and the ultrasonic bath was covered with a plastic black plate to prevent effect of sun lights. The temperature in all experiments was fixed at 25±3 ºC by the ultrasonic bath controller. Figure 1 shows the Fenton-Sonication system.

2.4 Analytical method

2.4.1 Chemical oxygen demand (COD)

COD is the amount of a particular oxidant that reacts with existing pollutants in a sample under controlled conditions. The concentration of chemical oxygen demand (COD) in the effluent was used to quantify the amount of organic compounds in the polluted stream. 2 ml of treated wastewater was digested with K₂Cr₂O₇ as an oxidizing agent for 2 hours at 150 ºC in a thermal reactor (Lovibond, RD125) to ascertain the COD value. The COD concentration was measured using a spectrophotometer, after bringing the digested sample to ambient temperature, The pH of an electrolyte was determined using a digital pH meter (ISOLAB Laborgerger GmbH, Germany). The effectiveness of COD removal was determined using (Equation 5) [27]:

\[
RE\% = \frac{COD_i - COD_f}{COD_i} \times 100
\]

\[\text{RE}\% \text{ is the removal efficacy, } COD_i \text{ is the initial COD (mg/L), and } COD_f \text{ is the final COD (mg/L).}
\]

Energy consumption was calculated by (Eq. 6) [28]:
\[ EC = \frac{P_{el} \times 1000}{V \times 60 \log \left( \frac{C_{OD_i}}{C_{OD_f}} \right)} \] ... (6)

EC is the energy consumption (kWh/m³), \( P_{el} \) denotes ultrasound power rates in (kW), \( t \) denotes time in (min), and \( V \) is the solution volume in (L).

### 2.4.2 The concentration of \( \text{H}_2\text{O}_2 \) generated in-situ by sonication

Using deionized water, experiments were done in the absence of the pollutant of interest to determine the amount of \( \text{H}_2\text{O}_2 \) generated in-situ by sonication.

A conical vessel containing 250 ml of pH-adjusted deionized water was immersed in an ultrasonic bath for 45 minutes. Throughout the experiment, samples were taken every fifteen minutes and analyzed using a titration with an aqueous potassium permanganate solution until a subtle pink shade was obtained. The chemical interaction is represented by the equation (Eq. 7) [29]:

\[
2\text{MnO}_4^- + 5\text{H}_2\text{O}_2 + 6\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{O}_2 + 8\text{H}_2\text{O} \] \( \ldots \) (7)

The \( \text{H}_2\text{O}_2 \) concentration was calculated using (Eq. 8) [29]:

\[
[H_2\text{O}_2] \text{ (mg/lit) } = \frac{5}{2} \times \frac{N_{kmno_4} \times V_{kmno_4}}{V_{H_2O_2}} \times 34 \times 1000 \] \( \ldots \) (8)

Where \( N_{kmno_4} \) is the molar concentration of \( kmno_4 \) solution (mol/L) and \( V_{kmno_4} \) and \( V_{H_2O_2} \) are the volumes of \( kmno_4 \) and the sample, respectively.

### 2.5 Experimental design

The central composite design (CCD) is the most prevalent design in the response surface methodology (RSM) method. The CCD is a fractional factorial design with five levels that is most commonly used to create second-order response surface models. This design consists of three types of points: cube points obtained from a factorial design, axial points, and the center point. \( N \) can be determined using the formula \( N = k^2 + 2k + n \), where \( k \) is the number of parameters and \( n \) is a number of repetitions [30].

The selected parameters in the current study were the \( \text{Fe}^{2+} \) dosage (X1), reaction time (X2) as the factors and COD removal rate (RE%) value as the response.

The process component scales have been identified as high (+1), median (0), and low (-1). Table 2 depicts the selected values for the process variables. As shown in Table 3, the Minitab-17 software was used to design the array of experiments for this investigation based on CCD.

<table>
<thead>
<tr>
<th>Table 2, Factors of the process in the refinery plant (coded and real levels).</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Process factors</strong></td>
</tr>
<tr>
<td>Coded levels</td>
</tr>
<tr>
<td>( \text{Fe}^{2+} ) dosage mM, (X1)</td>
</tr>
<tr>
<td>Reaction Time min, (X2)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 3, CCD design experimental array</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Run Order</strong></td>
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<tr>
<td></td>
</tr>
<tr>
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</tr>
<tr>
<td>2</td>
</tr>
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<td>3</td>
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<td>11</td>
</tr>
<tr>
<td>12</td>
</tr>
<tr>
<td>13</td>
</tr>
</tbody>
</table>
Response surface model or methodology describes the empirical model expressed as \( Y = F(x_1 + x_2 + \ldots + x_k) \). The first or second order polynomial models are utilized to develop a suitable approximation for \( F \) and are represented below. Regarding the 1st order model (Eq. 9):

\[
Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \varepsilon \quad \ldots (9)
\]

And for the 2nd order model (Eq. 10):

\[
Y = \beta_0 + \sum_{j=1}^{k} \beta_j x_j + \sum_{i=1}^{k} \beta_{ij} x_i^2 + \sum_{j=1}^{k-1} \sum_{i=2}^{k} \beta_{ji} x_j x_i + \varepsilon_i \quad \ldots (10)
\]

\( Y \) is the predicted response, \( \beta_0 \) is the constant, \( x_1, x_2, x_3, x_4 \) and \( x_5 \) are the operating variables, \( j, ji (j = 1, 2, \ldots, k; i = 1, 2, \ldots, k) \) and \( jj \) represent the regression coefficients of linear, interaction, and quadratic terms, respectively, and \( \varepsilon \) is the error. Typically, the quadratic model is suitable for RSM in the majority of instances. Therefore, models of the first or second order are sometimes refers to a regression models. In addition, fitting an acceptable response surface model involves statistical concepts, regression analysis methodologies, and optimization criteria [31].

3. Results and Discussion

3.1 Preliminary experiments for determination of in-situ generated \( \text{H}_2\text{O}_2 \) by Sonication

Ultrasonic irradiation of an aqueous solution generates \( \text{OH}^\bullet \) radicals and \( \text{H} \) radicals by cavitation (Eq. 1). The hydroxyl radical has a high oxidation potential and can directly oxidize organic substrates, leading to their decomposition or mineralization (Eq. 2) [32-33-34]. Nevertheless, hydroxyl radicals have a very limited lifetime and tend to bind to generate \( \text{H}_2\text{O}_2 \) (Eq. 4) [35, 36]. The production of hydrogen peroxide by ultrasonic irradiation at different time intervals and at fixed intensity and pH value of 3 is shown in Figure 2. It can be seen from Fig. 2 that the concentration of \( \text{H}_2\text{O}_2 \) is increased linearly with time. This result is predicted since many previous studies have demonstrated that, during sonication at constant intensity, the rate of hydroxyl radical formation may be considered to be constant, with hydrogen peroxide being a main result of sonication (Eq. 4 and Eq. 11) accumulating linearly in solution and serving as an \( \text{OH}^\bullet \) scavenger under ultrasonic irradiation [37-39]. Consequently, at the current study the rate of \( \text{H}_2\text{O}_2 \) generation is considered constant since ultrasonic intensity is also constant.

\[
2 \text{OOH} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad \ldots (11)
\]

Fig. 2. \( \text{H}_2\text{O}_2 \) in-situ generation by sonication.

3.2 Statistical Analysis of the Sono-Fenton results

Thirteen runs were performed in accordance with the CCD in order to find out and optimize the effects of process operating parameters on COD removal efficacy (RE%). Table 4 shows the number of runs, the experimental circumstances, the actual and estimated COD removal efficiency RE%.
Results in Table 4 showed that RE% is ranged between 65-90%. A comparison between run 8 and run 11 at the mid value of time (20 min) displays that Fe²⁺ dosage has the higher effect on COD removal with a maximum difference of 25% while at the mid value of Fe²⁺ dosage (0.2mM) effect of time is the lower with a maximum deference of 3% (runs 4 and 9). However, the real effect of each variable could be observed by ANOVA analysis.

The quadratic model regression was obtained by Minitab-17 software in terms of actual values (Eq. 12):

\[ RE\% = 33.09 + 225.9\, X_1 + 2.177\, X_2 - 410.8\, X_1^2 - 0.05613\, X_2^2 + 0.64\, X_1\, X_2 \quad \ldots (12) \]

Where \( X_1\) and \( X_2\) describe the interaction influence of model parameters and the double influences of model parameters \( X_1^2\) and \( X_2^2\) were utilized to determine the magnitude of their impact. The negative and positive coefficients in the model represent the negative and positive influence of experimental factors on COD elimination, respectively. As stated in Equation (12), the maximum coefficient belonged to \( X_1\) factor, implying that the double effect of Fe²⁺ dosage has the highest effect on the removal of COD during sono-Fenton process when compared to the other independent variables. In contrast, a low coefficient showed that double effect of reaction time \( X_2\) had the minimal effect on the response.

By graphing the anticipated versus actual data and the normal probability plot of the standardized residuals, the attractiveness and sufficiency of the model were also confirmed in Figure 3. It is evident from Figure 3 that there is a strong correlation between the experimental and estimated values, showing that the model was well-fitted and had a good ability to predict the COD removal rate RE%. No scattering with no definite pattern was observed, respecting the residuals revealing the significance of the model.

This may be interpreted as below [40]:

a) No Outliers exist in the data with respect to normal probability plot. This states that data are normally distributed and the RE% is affected by Fe²⁺ dosage and time.

b) A non-linear relationship was observed with respect to the plot of residuals versus fitted values plot confirming the variance is constant.

c) No skewing nor outliers were existed in Histogram.

d) An organized effects were observed in the data plot on residuals versus order due to time or data collection order.
In addition, the model's sufficiency and significance were evaluated using analysis of variance (ANOVA), and the results are shown in Table 6. The Model $R^2$ and $R^2_{adj}$ values of 96.40% and 92.20%, respectively, was relatively high, which indicates that the model obtained was able to give a convincingly good estimate of response in the studied range [41]. Furthermore, ANOVA table reveals that the present of contribution of the model was 95.68% and the linear term Contr.% is 57.03 in which $Fe^{2+}$ dosage (X1) Contr.% of 56.67 which represents the majority of the linear term with very week contribution of reaction time (X2) 0.36%.the week contribution of time could be results from nonlinear its behavior with RE%. The double (square) effect term contributes in the model was 38.45% while the interaction term was 0.21% only which is very insignificant. 

According to the ANOVA table, the model was extremely significant as the Fisher F test (F value) was determined to be 31.02 with a very low probability value (P value 0.0001), indicating that there was only a 0.01% chance that such a model could have been caused by noise [42].

Table 6.

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Seq SS</th>
<th>Contr. %</th>
<th>Adj SS</th>
<th>Adj MS</th>
<th>F-Value</th>
<th>P-Value</th>
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<tbody>
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<td>746.075</td>
<td>149.215</td>
<td>31.02</td>
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<td>444.669</td>
<td>57.03</td>
<td>444.669</td>
<td>222.334</td>
<td>46.22</td>
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<tr>
<td>X1</td>
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<td>56.67</td>
<td>441.867</td>
<td>441.867</td>
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<td>X2</td>
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<td>1.613</td>
<td>0.34</td>
<td>0.581</td>
</tr>
<tr>
<td>X1*X2</td>
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<td>1.613</td>
<td>0.21</td>
<td>1.613</td>
<td>1.613</td>
<td>0.34</td>
<td>0.581</td>
</tr>
<tr>
<td>Error</td>
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<td>33.672</td>
<td>4.32</td>
<td>33.672</td>
<td>4.810</td>
<td>0.34</td>
<td>0.581</td>
</tr>
<tr>
<td>Lack of Fit</td>
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<td>17.993</td>
<td>2.31</td>
<td>17.993</td>
<td>5.998</td>
<td>1.53</td>
<td>0.337</td>
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<tr>
<td>Pure error</td>
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<td>15.680</td>
<td>2.01</td>
<td>15.680</td>
<td>3.920</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>12</td>
<td>779.747</td>
<td>100.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Model Summary

$R^2$  96.40%
$R^2_{adj}$ 92.20%
$R^2_{pred}$ 80.45%

Fig. 3. Residual plots of COD removal rate by sono-Fenton.
3.3 Effect of operating factors on the sono-Fenton process

The surface plot combined with the contour plot was used to investigate the effect of Fe dosage and time on the COD removal efficiency, as shown in Figure 4 - a, b. It was clear that increasing Fe dosage results in increasing RE% to an optimum Fe dosage beyond which no further increase of RE% could occur. This behaviour occurs at any time. This can be interpreted as increasing the Fe$^{2+}$ dosage results in increase in the COD removal rate due to Fe$^{2+}$ reaction with the in-situ generated hydrogen peroxide according to (Eq. 3) [43].

Pang and his coauthors [44] stated that increasing Fe$^{2+}$ dosage would also increase the sono-Fenton process’s efficiency. Nevertheless, with increasing the Fe$^{2+}$ dosage more than the optimum value, self-quenching of •OH to produce Fe$^{3+}$ through (Eq. 13) could occur

$$\text{Fe}^{2+} + \text{OH} \cdot \rightarrow \text{Fe}^{3+} + \text{OH}^- \quad \text{... (13)}$$

Then, the resulting Fe$^{3+}$ can further react with H$_2$O$_2$ to form a complex intermediate (Fe (HO$_2$)$_2^{2+}$) (Eq. 14). Although (Fe (HO$_2$)$_2^{2+}$) can be spontaneously decomposed to Fe$^{2+}$ and •OOH, the decomposition rate was much lower. The decomposition rate of (Fe (HO$_2$)$_2^{2+}$) can be greatly enhanced under ultrasonic irradiation (Eq. 15). A cycle mechanism is established once the isolated Fe$^{2+}$ further reacts with H$_2$O$_2$ to produce •OH (Eq. 3) [45, 46].

$$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe} - \text{O}_2\text{H}_2^+ + \text{H}^+ \quad \text{... (14)}$$

Several studies had investigated the effect of iron dosage on the sono-Fenton process, and the majority of researchers have concluded that the degradation of pollutants by the sono-Fenton process increased significantly with the addition of Fe$^{2+}$ [47-50]. On the whole, the addition of Fe$^{2+}$ is generally beneficial for the acceleration of organic compound degradation; however, an excessive dosage of Fe$^{2+}$ will decrease treatment efficiency due to the reduction of OH• caused by the addition of excessive Fe$^{2+}$ (Eq. 13) [50-52]. Consequently, higher iron dosages are only advantageous under specific conditions.

According to previous studies, reaction time is one of the most crucial parameters affecting hybrid wastewater treatment systems [53, 54]. Based on Figure 4-a, the RE% increases with increasing time up to 20 min then starts to decrease. According to data concerning the effect of reaction time, as the time climbed from 20 to 34.14 min at constant Fe$^{2+}$ dosage 0.2 mM, the rate of removal decreased by 9.02%. This is probably because the in-situ generated hydrogen peroxide by sonication was partially consumed [55]. This behavior was happen at any value of Fe dosage.

In the majority of previous literature reviews, it was found that the COD removal rate increases as the reaction time increased. This behaviour is expected due to the increased production of hydroxyl radicals OH• during sonication [31, 14, 56-58].

In contrast, in the current study, increasing the reaction time beyond 20 minutes will decrease the COD removal rate, which is an unpredicted result consistent with a small number of previous findings [59-61]. Yosofi and Mousavi [62] attributed that the decrease of RB5 removal rate happened when the concentration of H$_2$O$_2$ elevated to 400 mg/l due to the consumption of OH• radicals by extra hydrogen peroxide at high concentration instead of reacting with RB5 Eqs. (16, 17, 18),

$$\text{OH} \cdot + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 \cdot + \text{H}_2\text{O} \quad \text{... (16)}$$

$$\text{HO}_2 \cdot + \text{OH} \cdot \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad \text{... (17)}$$

$$\text{H} \cdot + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 \cdot + \text{H}_2\text{O} \quad \text{... (18)}$$

However, the rate of H$_2$O$_2$ generation at the current study was considered constant, authors suggest that the OH• radicals instead of attacking the organic pollutant, it will continue producing H$_2$O$_2$ overtime and hence accumulating it in the solution which results in consuming OH• (Eq. 16, 17, 18) in the same behavior of [62] when authors increased the concentration of H$_2$O$_2$. In addition, the accumulated hydrogen peroxide may function as a hydroxyl radical scavenger, resulting in the production of hydro-peroxy radicals that are less reactive than hydroxyl radicals (Eq. 19) [61].

$$\text{H}_2\text{O}_2 + \text{OH} \cdot \rightarrow \text{HO}_2 \cdot + \text{H}_2\text{O} \quad \text{... (19)}$$
Fig. 4. The interaction effect of Fe dosage and time on the COD removal. a)surface plot, b) contour plot.

The contour plot is significant to detect the reign of optimum values. As shown in Figure 4-b, the higher removal rate with RE% higher than 85% could be attained only at Fe dosage greater than 0.2 mM and time in the range (15-25min), hence the optimization results should be lied with this scope.

3.4 Optimization

The primary objective of CCD-based RSM was to identify the ideal operating parameters for maximizing the percent of COD removal efficiency in the treatment of petroleum refinery wastewater by the hybrid process (sono-Fenton).

Minitab-17 software was used to maximize the COD RE%, taking into account the variety of examined parameters and their responses as shown in Tables 2 and 5, respectively. Within these constraints and parameters, the optimization technique was carried out, and the results are displayed in Table 7 and Figure 5.

For confirmation, an experiment was conducted utilizing the improved parameters. Besides, for comparing the efficiency of combining ultrasound irradiation with Fenton reaction, three more experiments were done (sonolysis, classical Fenton, and sono-Fenton with addition of H₂O₂ externally). Table 8 provides the results. After approximately 21 minutes of the sono-Fenton process, the COD removal efficiency at pH=3 was 85.81% (in the range of the optimal value determined by optimization analysis with a DF of 1) (Table 6). Consequently, employing CCD in conjunction with DF is effective and efficient for maximizing COD elimination using sono-Fenton hybrid advanced oxidation method. Based on the present method, the final COD concentration was (65ppm) which is lower than the value of the effluent discharge from the
biological unit (102 ppm) used in the Al-
Diewanya refinery plant and is in agreements with
the standard level for discharging of wastewaters
globally.

External addition of H$_2$O$_2$ to sono-Fenton was
found to decrease the COD removal rate to be
57.68% and a dark yellow color of the solution
after treatment was observed. This could be due
to the reaction between excessive H$_2$O$_2$ and OH•
according to (Eq. 19), which results in the
creation of HO$_2$•, which has insignificant
oxidative strength in comparison to hydroxyl free
radicals [63, 64]. At greater concentrations of
hydrogen peroxide, H$_2$O$_2$ served as an interfering
agent and reacted with hydroxyl radicals OH• in
the aqueous medium, thereby limiting their attack
on contaminant molecules [64]. In addition,
sonolysis alone and classical Fenton process give
removal efficiency of 64.84% and 56%
respectively which is also lower than the hybrid
sono-Fenton process removal. This is because of
the increased number of hydroxyl radicals
generated by sono-Fenton, therefore, the rate of
breakdown and oxidation of organic matter will
also increase. Since the number of radicals
derived from H$_2$O$_2$ in the hybrid system is greater
than in an isolated sonication system, the rate of
oxidation will be greater in the hybrid system
[65].

Table 7. Response Optimization: RE%

<table>
<thead>
<tr>
<th>Response</th>
<th>Target</th>
<th>Lower</th>
<th>Upper</th>
<th>Weight</th>
<th>Importance</th>
</tr>
</thead>
<tbody>
<tr>
<td>RE (%)</td>
<td>Max</td>
<td>65</td>
<td>90</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Parameters

<table>
<thead>
<tr>
<th>Fe$^{2+}$ (mM)</th>
<th>Time (min)</th>
<th>Fit</th>
<th>SE</th>
<th>95% CI</th>
<th>95% PI</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.29</td>
<td>21</td>
<td>88.90</td>
<td>1.06</td>
<td>86.38-91.41</td>
<td>83.14-94.66</td>
</tr>
</tbody>
</table>

![Diagram](image)

Fig. 5. Optimization plot

Table 8. Confirmative run with comparison with related processes

<table>
<thead>
<tr>
<th>Run</th>
<th>Case</th>
<th>Fe$^{2+}$ (mM)</th>
<th>Time (min)</th>
<th>H$_2$O$_2$</th>
<th>COD (ppm)</th>
<th>RE%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sono-Fenton</td>
<td>0.29</td>
<td>21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Sono-Fenton with addition of</td>
<td>0.29</td>
<td>21</td>
<td>2.9 mM</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>H$_2$O$_2$ externally</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Sonolysis only</td>
<td>-</td>
<td>21</td>
<td></td>
<td>458</td>
<td>64.84</td>
</tr>
<tr>
<td>4</td>
<td>Classical Fenton process</td>
<td>0.29</td>
<td>21</td>
<td></td>
<td>458</td>
<td>56.55</td>
</tr>
</tbody>
</table>
3.5 Comparison with previous works

The results of the current study were compared to prior research in the same field in Table 9. It demonstrates that the current results are favorable in terms of the high removal rate in a brief amount of time, approximately 20 minutes, the lack of energy consumed, and the low cost, which encourages the adoption of the current method for treating polluted water from sources other than oil refineries, such as textile and cosmetics factories.

<table>
<thead>
<tr>
<th>Table 9. Comparison with previous works</th>
</tr>
</thead>
<tbody>
<tr>
<td>process</td>
</tr>
<tr>
<td>Degradation of phenol in aqueous solution by fenton, sono-fenton and sono-photo-fenton methods</td>
</tr>
<tr>
<td>Ozone (O3) and sono (US) based advanced oxidation processes for the removal of color, COD for landfill leachate</td>
</tr>
<tr>
<td>Treatment of petroleum effluents using the combined ultrasound and Fenton oxidation process</td>
</tr>
<tr>
<td>The production of sono-Fenton System by Trace ferrous ion addition in sono-degradation Dimethoate</td>
</tr>
<tr>
<td>Petroleum refinery wastewater /sonofenton</td>
</tr>
</tbody>
</table>

4. Conclusion

In this research, combining of ultrasound irradiation and Fenton as a hybrid process was investigated to treat real petroleum refinery wastewater. The optimum operation variables were found by response surface methodology (RSM) with central composite design (CCD). A maximum concentration of H₂O₂ that generated in-situ by sonication was found to be 8.5 mg/l at 45min and its rate was constant throughout all experiments. The optimal RE% for sono-Fenton process was 85.81% obtained at 21 minutes and Fe²⁺ dosage of 0.289. Analysis of variance (ANOVA) showed that the model R² is 96.40% and the Fe²⁺ dosage is the main factor that greatly affects the treatment process. The results revealed that the efficiency of the individual classical Fenton process and sonolysis process were low. In contrast, when Fenton is combined with sonication, the removal efficiency is considerably enhanced. Adding external H₂O₂ has an adverse effect on the COD removal which decreased by 27.95%. Furthermore, the utilizing hybrid process give final COD concentration of 65ppm which is lower than the value of COD of effluent discharged from the biological unit used in the Al-Diewanya refinery plant.

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5. References


removal from petroleum product feedstock. Ultrasonics sonochemistry, 16(6), 732-736.


معالجة المياه العادمة الخارجة من مصافي النفط بأعتماد عملية السونوفنتون وباستثمار بيروكسيد الهيدروجين المتولد آلياً من الموجات فوق الصوتية

علي حسين عبار

قسم الهندسة الكيميائية الاحيائية/ كلية الهندسة الخوارزمي/ جامعة بغداد

البريد الإلكتروني: Marwa.jeyad2205m@kecbu.uobaghdad.edu.iq

الخلاصة

تقدم هذه الدراسة طريقة جديدة لمعالجة المياه العادمة الخارجة من المصافي النفطية. تم اختيار مقياس حذف الأكسجين (COD) كمقياس هدف. تم استخدام البرنامج الإحصائي منهجية سطح الاستجابة (RSM) بالاعتماد على التصميم المركزي المركزي (CCD) للحصول على أفضل نسبة حذف RE. تم دراسة اثنين من العوامل الرئيسية على العملية (RSM) باستخدام التصميم المركزي المركزي (CCD). تم الحصول على أعلى نسبة حذف RE وهي 85.81% في الظروف المثالية لمدة 21 دقيقة و0.289 مولارات من Fe²⁺. أظهرت النتائج أن تركيز Fe²⁺ له أكبر تأثير على حذف COD، يليه وقت التفاعل. أثبتت قيمة R² المربعة (96.40%) صحة النموذج وللمعادلة، واعتمد الناجح في معالجة المياه العادمة من مصافي النفط. أظهرت مقارنة بين عملية سونوفنتون التي تم إجرائها بالاعتماد على الكمية المتولدة داخليا من بيروكسيد الهيدروجين عن طريق الموجات فوق الصوتية وبيروكسيد الهيدروجين كعملية مجهزة عن طريق الإضافة الخارجية أن أفضل عملية للإزالة هي العملية المشتركة السونوفنتون التي تم إجرائها بدون إضافة بيروكسيد الهيدروجين خارجيا وأن هذه العملية أفضل من العملية المجهزة الكلاسيكية كافقة فقط أو الصوتة فقط.