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

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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 Fe^{2+} concentration. Additionally, the results revealed that the concentration of Fe^{2+} 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 (SO_4•) are generated to remove refractory organic matters, trace organic contaminants, or certain inorganic pollutants or to increase wastewater bio-degradability 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].

$$H_2O +))) \rightarrow OH \bullet + H \bullet \qquad \ldots (1)$$
$$\text{Organic pollutant} + OH \bullet \rightarrow CO_2 + H_2O$$
$$\ldots (2)$$
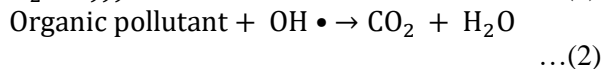
Where:-))) denotes to the ultrasound waves.

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].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH \bullet \qquad \ldots (3)$$
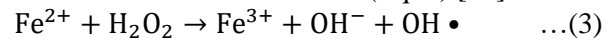
The Fenton method is favoured among AOPs because it is user-friendly, has a short reaction time, and runs at room temperature and pressure, making it more cost-effective. In addition, it had other disadvantages, including a narrow pH range and an excessive amount of iron sludge [20]. To overcome classical 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].

$$2 \, OH \bullet \rightarrow \ H_2O_2 \qquad \qquad \ldots (4)$$

It is worth noting that all local works done in sono-Fenton, were done by adding H_2O_2 externally, and only a few global works were done depending on the in-situ sono-generated H_2O_2.

This study focuses on the combined application of ultrasound and the Fenton process for treating natural petroleum refinery wastewater from the Al-Diwaniya 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-Diewanya refinery. Prior to the biological treatment stage, 15L of effluents were been obtained from the storage tank and refrigerated at 4ºC 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

Characteristic	Initial	Final	Unit
pH	6.6	7.3	
Temperature	25	22	ºC
TDS	5566	4898	ppm
Phenol	18.5	0.05	ppm
COD	550	102	ppm
BOD	180	20	ppm
Oil	25.2	11.6	mg/L
Turbidity	33	7.29	NTU
PO_4^{3-}	0.12	0.8	Ppm
Cl^-	900	450	Ppm

2.2 Chemicals

Ferrous sulfate (FeSO_4.7H$_2O$; 99% pure) and hydrogen peroxide (H$_2O_2$,35%) were used as Fenton's reagents and the pH of solution was adjusted using sulfuric acid (1M) and sodium hydroxide (1M). Potassium Permanganate (KMnO$_4$) employed in a titration to estimate the concentration of H$_2O_2$ 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 H_2SO_4 , 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.
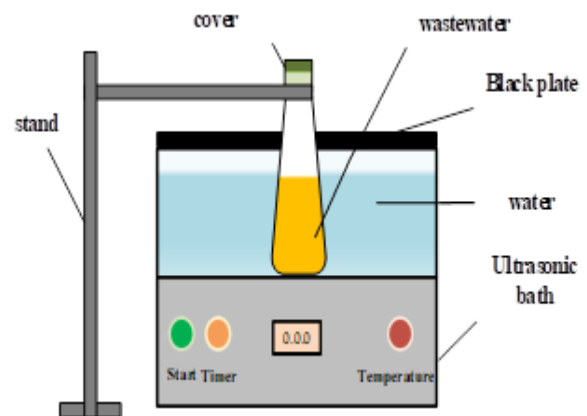

Fig. 1. Fenton-Sonication system.

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 $K_2Cr_2O_7$ as an oxidizing agent for 2 hours at 150 °C 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]:

$$RE\% = \frac{COD_i - COD_f}{COD_i} \times 100 \qquad ...(5)$$

RE% is the removal efficacy, COD$_i$ is the initial COD (mg/L), and COD$_f$ is the final COD (mg/L). Energy consumption was calculated by (Eq. 6) [28]:

$$E\,C = \frac{P_{el} \times t \times 1000}{V\,60\log(\frac{COD_i}{COD_f})} \qquad \ldots(6)$$

EC is the energy consumption (kWh/m^3), 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 H_2O_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 H_2O_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]:

$$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow Mn^{2+} + 5O_2 + 8H_2O \qquad \ldots(7)$$
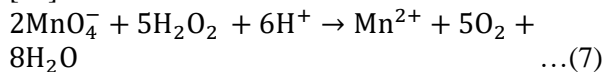
The H_2O_2 concentration was calculated using (Eq. 8) [29]:

$$[H_2O_2]\ \ (mg/lit) = \frac{5}{2} \times \frac{N_{kmno4} \times V_{kmno4}}{V_{H2O2}} \times 34 \times 1000 \qquad \ldots (8)$$

Where N_{kmno4} is the molar concentration of $kmno_4$ solution (mol/L) and V_{kmno4} and V_{H2O2} 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 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 2,
Factors of the process in the refinery plant (coded and real levels).

Process factors	Range in CCD				
Coded levels	-α	Low (-1)	Middle (0)	High (+1)	+α
Fe^{2+} dosage mM, (X1)	0.0586	0.1	0.2	0.3	0.3414
Reaction Time min, (X2)	5.8579	10	20	30	34.142

Table 3,
CCD design experimental array

Run Order	Blocks	Coded Values		Real values	
		x_1	x_2	Fe^{2+} dosage (mM),X1	Reaction Time (min),X2
1	1	+1	-1	0.3000	10.000
2	1	0	0	0.2000	20.000
3	1	0	0	0.2000	20.000
4	1	0	+α	0.2000	34.142
5	1	+1	+1	0.3000	30.000
6	1	-1	-1	0.1000	10.000
7	1	0	0	0.2000	20.000
8	1	+α	0	0.3414	20.000
9	1	0	-α	0.2000	5.8579
10	1	-1	+1	0.1000	30.000
11	1	-α	0	0.0586	20.000
12	1	0	0	0.2000	20.000
13	1	0	0	0.2000	20.000

Response surface model or methodology describes the empirical model expressed as $Y = F(x_1 + x_2 +... + x_k)$. 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):

$$Y = \beta_\circ + \sum_{j=1}^{k} \beta_j x_j + \varepsilon \qquad \qquad \dots (9)$$

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

$$Y = \beta_\circ + \sum_{j=1}^{k} \beta_j x_j + \sum_{j=1}^{k} \beta_{jj} x_j^2 +$$
$$\sum_{j=1}^{k-1} \sum_{i=2}^{k} \beta_{ji} x_j x_i + \varepsilon_i \qquad \dots (10)$$

Y is the predicted response, $\beta_\circ$ is the constant, x_1, x_2, x_3, x_4 and x_5 are the operating variables, j, ji (j = 1, 2,..., k; I = 1, 2,..., k) and jj represent the regression coefficients of linear, interaction, and quadratic terms, respectively, and ε 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 H_2O_2 by Sonication

Ultrasonic irradiation of an aqueous solution generates OH• radicals and 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 H_2O_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 H_2O_2 is increased

linearly with time. This result is predicted since many previous studies has 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 OH• scavenger under ultrasonic irradiation [37-39]. Consequently, at the current study the rate of H_2O_2 generation is considered constant since ultrasonic intensity is also constant.
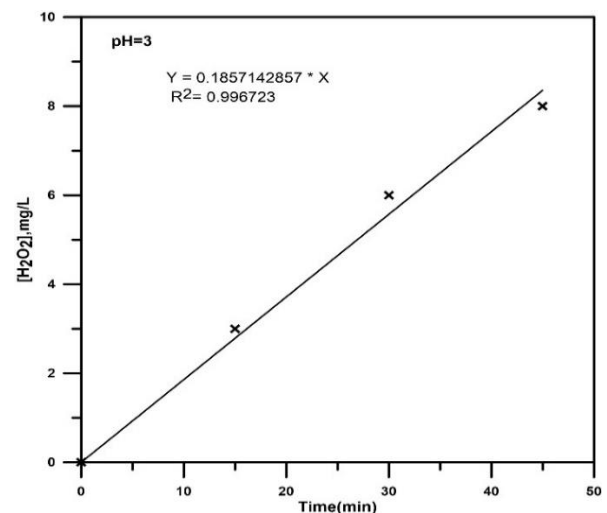
$$2\,OOH \rightarrow H_2O_2 + O_2 \qquad \qquad \dots (11)$$

Fig. 2. H_2O_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%.

Table 4,
CCD results

Run Order	Blocks	Fe dosage(mM)	Time (min)	RE%Actual	RE% Predicted
1	1	0.3000	10.000	80.78	81.9626
2	1	0.2000	20.000	86.89	85.4780
3	1	0.2000	20.000	85.00	85.4780
4	1	0.2000	34.142	75.98	75.0894
5	1	0.3000	30.000	82.31	84.4162
6	1	0.1000	10.000	70.00	68.3688
7	1	0.2000	20.000	83.00	85.4780
8	1	0.3414	20.000	90.00	87.7728
9	1	0.2000	5.8579	73.00	73.4156
10	1	0.1000	30.000	68.99	68.2824
11	1	0.0586	20.000	65.00	66.7522
12	1	0.2000	20.000	88.00	85.4780
13	1	0.2000	20.000	84.50	85.4780

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 Fe^{2+} dosage has the higher effect on COD removal with a maximum difference of 25% while at the mid value of Fe^{2+} 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 X1 + 2.177 X2 - 410.8 X_1^2 - 0.05613 X_2^2 + 0.64 X1*X2 …(12)

Where X1*X2 describe the interaction influence of model parameters and the double influences of model parameters $(X1)^2$ and $(X2)^2$ 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 (X1*X1) factor, implying that the double effect of Fe^{2+} 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 (X2*X2) 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 Fe^{2+} 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.
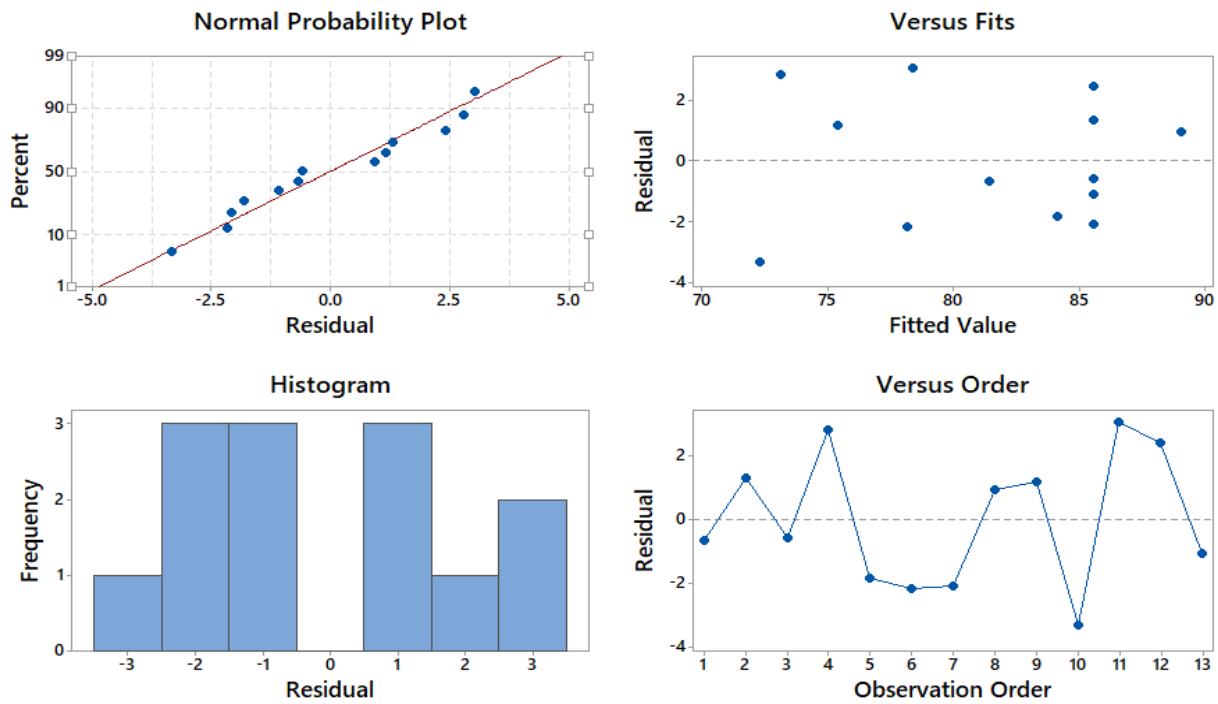
Fig. 3. Residual plots of COD removal rate by sono-Fenton.

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 $R^2 adjusted$ 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.
Analysis of Variance results

Source	DF	Seq SS	Contr. %	Adj SS	Adj MS	F-Value	P-Value
Model	5	746.075	95.68	746.075	149.215	31.02	0.000
Linear	2	444.669	57.03	444.669	222.334	46.22	0.000
X1	1	441.867	56.67	441.867	441.867	91.86	0.000
X2	1	2.808	0.36	2.802	2.802	0.58	0.470
Square	2	299.793	38.45	299.793	149.896	31.16	0.000
X1*X1	1	80.642	10.34	117.382	117.382	24.40	0.002
X2*X2	1	219.151	28.11	219.151	219.151	45.56	0.000
2-Way Interaction	1	1.613	0.21	1.613	1.613	0.34	0.581
X1*X2	1	1.613	0.21	1.613	1.613	0.34	0.581
Error	7	33.672	4.32	33.672	4.810		
Lack of Fit	3	17.993	2.31	17.993	5.998	1.53	0.337
Pure error	4	15.680	2.01	15.680	3.920		
Total	12	779.747	100.00				

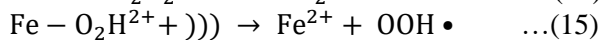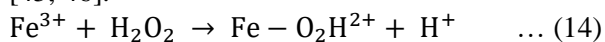| Model Summary		R^2		R^2(adj.)		R^2(pred.)	
		96.40%		92.20%		80.45%	

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 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

$$Fe^{2+} + OH\bullet \rightarrow Fe^{3+} + OH^- \qquad \dots (13)$$
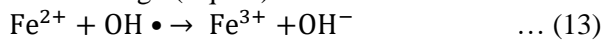
Then, the resulting Fe^{3+} can further react with H_2O_2 to form a complex intermediate (Fe $(HO_2)^{2+}$) (Eq. 14). Although (Fe $(HO_2)^{2+}$) can be spontaneously decomposed to Fe^{2+} and •OOH, the decomposition rate was much lower. The decomposition rate of (Fe $(HO_2)^{2+}$) can be greatly enhanced under ultrasonic irradiation (Eq. 15). A cycle mechanism is established once the isolated Fe^{2+} further reacts with H_2O_2 to produce •OH (Eq. 3) [45, 46].

$$Fe^{3+} + H_2O_2 \rightarrow Fe - O_2H^{2+} + H^+ \qquad \dots (14)$$
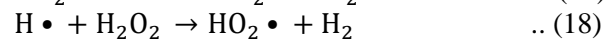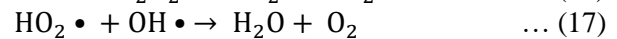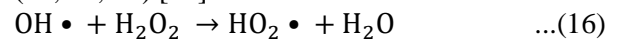$$Fe - O_2H^{2+} +))) \rightarrow Fe^{2+} + OOH\bullet \qquad \dots(15)$$

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 increased 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_2O_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) [62].

$$OH\bullet + H_2O_2 \rightarrow HO_2\bullet + H_2O \qquad \dots(16)$$
$$HO_2\bullet + OH\bullet \rightarrow H_2O + O_2 \qquad \dots (17)$$
$$H\bullet + H_2O_2 \rightarrow HO_2\bullet + H_2 \qquad \dots (18)$$

However, the rate of H_2O_2 generation at the current study was considered constant, authors suggests that the OH• radicals instead of attacking the organic pollutant, it will continue producing H_2O_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_2O_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].
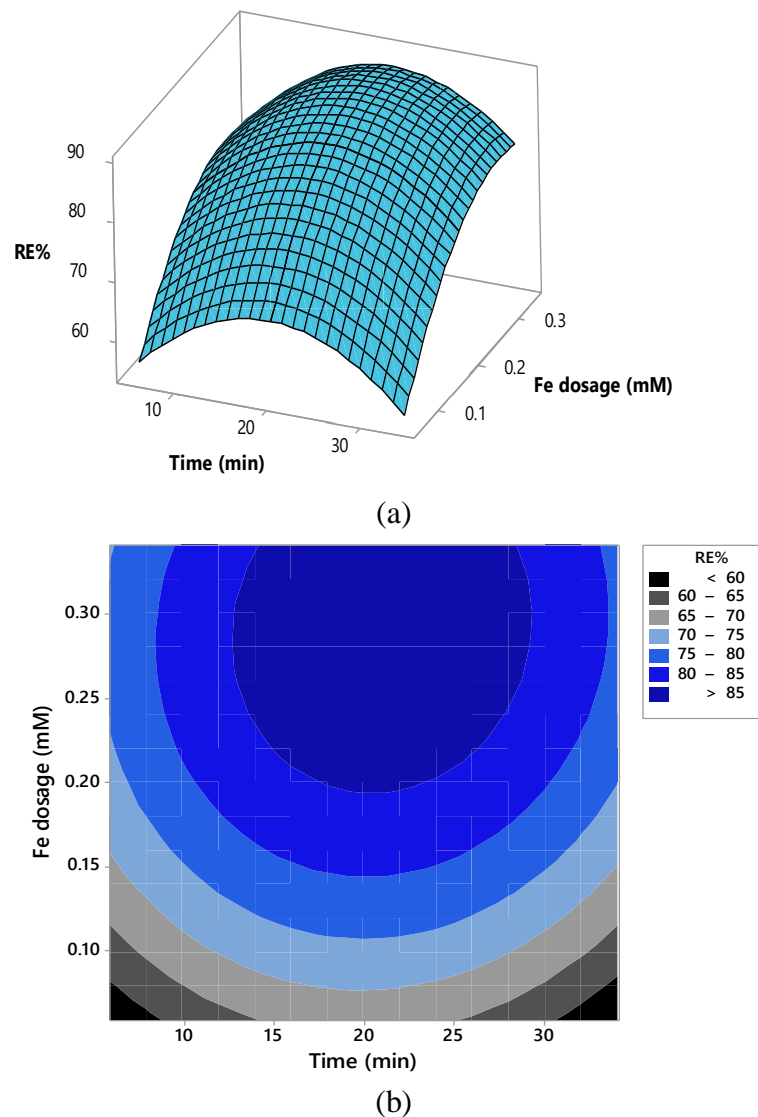
$$H_2O_2 + OH\bullet \rightarrow HO_2\bullet + H_2O \qquad \dots (19)$$

(a)

(b)
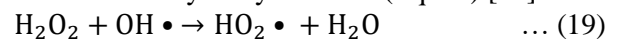
Fig. 4. The interaction effect of Fe dosage and time on the COD removal. a)surface plot, b) contour plot.

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 H_2O_2 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 D_F 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_2O_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_2O_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_2O_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_2O_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%

Response	Target	Lower	Upper	Weight	Importance
RE (%)	Max	65	90	1	1

Parameters

Fe^{2+} (mM)	Time (min)	Fit	SE Fit	95% CI	95% PI
0.29	21	88.90	1.06	86.38-91.41	83.14-94.66
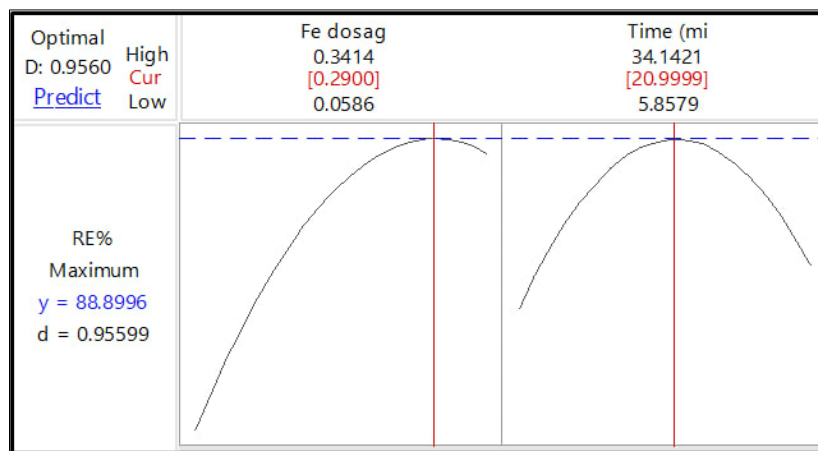
Fig. 5. Optimization plot

Table 8.
Confirmative run with comparison with related processes

Run	Case	Fe^{2+} (mM)	Time (min)	H_2O_2	COD (ppm) initial	COD (ppm) final	RE%
1	Sono-Fenton	0.29	21		458	65	85.81
2	Sono-Fenton with addition of H_2O_2 externally	0.29	21	2.9mM	458	193	57.86
3	Sonolysis only	-	21		458	161	64.84
4	Classical Fenton process	0.29	21		458	199	56.55

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 9.
Comparison with previous works

process	Conditions	optimum	Reference
Degradation of phenol in aqueous solution by fenton, sono-fenton and sono-photo-fenton methods	Phenol 200mg/l, Fe^{2+}=30 mg/l, H_2O_2=800mg/l, pH=3,time=60min temperature =30° C	RE%=58.2	[22]
Ozone (O3) and sono (US) based advanced oxidation processes for the removal of color, COD for landfill leachate	Fe^{2+}=30mM pH=7,time=180 min temperature =30° C	For US/ Fe^{2+}/H_2O_2 RE%=40 EC=216kWh /m^3	[66]
Treatment of petroleum effluents using the combined ultrasound and Fenton oxidation process	H_2O_2/Fe^{2+}=10 pH=3, time=10 min	RE%=84.25	[67]
The production of sono-Fenton System by Trace ferrous ion addition in sono-degradation Dimethoate	Fe^{2+}=0.2mM pH=3,time=10 min temperature =30C	RE%=95.3	[25]
Petroleum refinery wastewater /sonofenton	Fe^{2+}=0.289 mM pH=3,time=21 min temperature =30C	RE%=85.81 EC=90.57k Wh/m^3	Present study

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 H_2O_2 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 Fe^{2+} dosage of 0.289. Analysis of variance (ANOVA) showed that the model R^2 is 96.40% and the Fe^{2+} 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 H_2O_2 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.

Acknowledgment

5. References

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معالجة المياه العادمة الخارجة من مصافي النفط بأعتماد عملية السونوفنتون وبأستثمار بيروكسيد الهيدروجين المتولد آنيًا من الموجات الفوق الصوتية

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الخلاصة

تقدم هذه الدراسة طريقة جديدة لمعالجة المياه العادمة الخارجة من المصافي النفطية من خلال الجمع بين الموجات فوق الصوتية وعملية الفنتون كعملية سونو-فنتون. تم اختيار ازالة الطلب الكيميائي للأوكسجين (COD) كدالة هدف (RE%) . تمت دراسة اثنين من العوامل المؤثرة الرئيسية على العملية باستخدام البرنامج الاحصائي منهجية سطح الاستجابة Respone surface methodology (RSM) مع اعتماد التصميم المركب المركزي (CCD) Central Composite design. تم الحصول على أعلى نسبة ازالة RE ٪ وهي 85.81٪ في الظروف المثالية لمدة 21 دقيقة و 0.289 ملي مولار من الحديد Fe²⁺ بالإضافة إلى ذلك ، أوضحت النتائج أن تركيز Fe²⁺ له أعلى تأثير على التخلص من COD ، يليه وقت التفاعل . أثبتت قيمة R² المرتفعة (96.40٪) صحة التوافق القوي لمعادلة النموذج والاعتماد الناجح لـ RSM في معالجة المياه العادمة من مصافي البترول . علاوة على ذلك ، أظهرت مقارنة بين عملية سونو-فنتون التي تم اجرائها بالاعتماد على الكمية المتولدة داخليًا من بيروكسيد الهيدروجين عن طريق الموجات فوق الصوتية وبين عملية سونو-فنتون أخرى تم اجراءها عن طريق الاضافة الخارجية لبيروكسيد الهيدروجين وايضا عملية الفنتون الكلاسيكية وSonolysis عملية الصوتنة الاعتيادية بدون اضافة الحديد وبيروكسيد الهيدروجين أن أفضل عملية للإزالة هي العملية المشتركة السونو-فنتون التي تم اجراءها بدون اضافة بيروكسيد الهيدروجين خارجيا وان هذه العملية افضل من العمليات الفردية الكلاسيكية كالفنتون فقط او الصوتنة فقط.