

# Treatment of Refinery Wastewater by Chemical Advanced Oxidation Processes (UV-Photolysis, Fenton, and Photo-Fenton): A Comparative Study

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**ABSTRACT:** A huge amount of oily wastewater is discharged from industrial activities, especially the refinery plants. Therefore, scientists focus their research on the investigation of effective methods to treat this kind of wastewater. This work investigates and compares the effectiveness of chemical advanced oxidation techniques to remediate real refinery wastewater generated from the Al-Samawa refinery plant which has not been treated before by using the present technologies. Real refinery wastewater underwent a batch photo-Fenton oxidation treatment (UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>) to reduce the oil content. The experiments were designed using a factorial experimental design containing the effects of 30-90 min irradiation time, 25–250 ppm hydrogen peroxide, and 2–8.5 pH. A statistical program was used to analyze the results. The optimum values of these variables were 90 min, 100 ppm H<sub>2</sub>O<sub>2</sub>, and pH 3. The effect of solution temperature on the removal efficiency was studied in the range of 20–400 °C. It was found that the temperature notably influences the treatment process, where the highest removal of the organic content of 95.15% was achieved at 30°C. Adsorption equilibrium investigation revealed that the Langmuir model was a more fitted model ( $R^2 = 0.9999$ ) for photo-Fenton elimination of oil content than other isotherm models. Consequently, a comparative study of the treatability of UV-photolysis, Fenton, and photo-Fenton processes has been conducted. The core findings of this comparison showed that the oil content removal by using the UV-photolysis process is (49.2%), the Fenton process (69.6%, while it shows that the photo-Fenton process is the most effective at getting rid of pollutants (92.75%). As observed the photo-Fenton methods are more effective than other studied methods to treat refinery wastewater.

**KEYWORDS:** AOPs treatment methods; Adsorption isotherms; ANOVA analysis; Kinetic study.

## INTRODUCTION

The environmental influence of petroleum industries is frequently harmful; meanwhile, they consume a considerable

quantity of water and discharge notable amounts of oily wastewater. There is a growing understanding of the need

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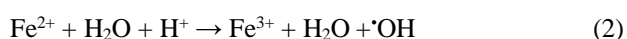
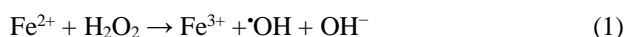
to avoid the pollution caused by oil refinery waste streams since organic demand is predicted to expand over the next 20 years [1-3]. Wastewater discharged from oil refining activities differs from one industry to another depending on the type of treated crude oil. These wastewaters involve numerous organic and inorganic materials, for example, dissolved oil, ammonia, dyes, and heavy metals [4-10]. As demonstrated, water cannot dissolve most organic molecules, which will be dispersed in water [11-14].

Most current approaches for eliminating organic pollutants from real Refinery WasteWater (RWW) are ineffective in meeting the criteria for oily wastewater discharged [15]. Adsorption, chemical participation, and membrane processes are some types of conventional methods that are performed to treat several types of wastewaters [2,3,16-20]. These approaches are inadequate for producing clean water with an acceptable limit of the most toxic contaminants. Further treatment methods are frequently essential to reach this goal.

Advanced Oxidation Processes (AOPs) have been employed to overcome the disadvantages observed in the conventional methods [21-26]. Under acceptable restrictions, the oxidation processes may convert organic pollutants into harmless inorganic chemicals like CO<sub>2</sub> and H<sub>2</sub>O [27]. Advanced oxidation processes are physicochemical technologies in nature that release extremely oxidizing species, mainly free radical ( $\bullet$ OH) [25,28,29]. Advanced chemical technologies involving Fenton reagent (H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>), photo-Fenton reaction (UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> or Fe<sup>3+</sup>), peroxidation (O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>), O<sub>3</sub> photolysis (UV/O<sub>3</sub>), and photolysis of H<sub>2</sub>O<sub>2</sub> (UV/H<sub>2</sub>O<sub>2</sub>) [29-31].

### Fenton method

The Fenton process (Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub>) is the oldest method of the chemical AOP, which is applied to eliminate persistent organic pollutants (POPs). The mechanism of the Fenton process is dependent on the generation as shown in Eq. (1) based on the conditions of pH, temperature, Fe(II) concentration, and H<sub>2</sub>O<sub>2</sub>. The reaction shown in Eq. (1) takes place in an acidic medium (about 2.8–3.0); therefore, it can be written as presented in Eq. (2) [32, 33]:



However, in the acidic medium, Fenton's reaction required a small amount of Fe(II) which is reformed from the Fenton-like reaction between Fe(III) and H<sub>2</sub>O<sub>2</sub> (Eq. (3))

where the HO<sub>2</sub><sup>•</sup> radical is less reactive with organic compounds compared to  $\bullet$ OH and the Fenton's reaction is more rapid than Fenton-like reaction [32]:



The main advantages of the Fenton process are its flexibility of operation, inexpensive chemicals required, and no energy input needed. However, it suffered from risks due to the transportation of hydrogen peroxide, the accumulation of the sludge containing iron, and the formation of complex materials, such as iron (III)-carboxylic acid [24, 29].

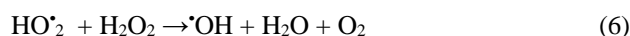
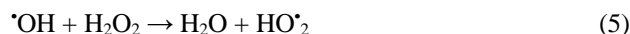
### UV-photolysis method

UV radiation can be used to photolyze H<sub>2</sub>O<sub>2</sub> at a range of wavelengths from 200 to 300 nm, leading to the generation of ( $\bullet$ OH) radicals [25]. These radicals can also decompose the hydrogen peroxide by secondary reactions as follows [29,33]:

- The initiation step:



- The propagation steps:



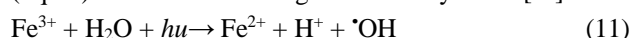
- The termination steps:



However, the disadvantage of the drawback of the UV-photolysis method is the lower molar absorption coefficient of hydrogen peroxide in the UV region which means that a rather strong concentration of H<sub>2</sub>O<sub>2</sub> provides an efficient oxidation process of the organic contaminants [29, 32].

### photo-Fenton method

When the Fenton reaction (Eq. (1)) is photo-assisted by performing UV radiations, the catalytic reduction, in hydrogen peroxide aqueous solution, of Fe(III) into Fe(II) will be too excited, which raises the generation of hydroxyl radicals (Eq. 11) based on the wavelength and intensity of UV [33]:



**Table 1: Specification of Refinery Waste Water (RWW) used in this study**

Parameters	Values	Parameters	Values
Oil content	60.5 (mg/l)	Conductivity	100451 $\mu\text{s}/\text{cm}$
Turbidity	53.2 NTU	TDS	64346.24 (mg/l)
pH	6.92	Viscosity	1.0504 m Pa/S
Solution oxygen content	0.055 (mg/l)	Iron	0.39 (mg/l)
Specific gravity	0.992	Sulphate	62.7 (mg/l)

At the acidic medium of (2.8–3.5), the distinguished form of Fe(III) is the  $[\text{Fe}(\text{OH})]^{2+}$  ion which plays an essential object in the photo-Fenton process. The generation of hydroxyl radicals via the photo-Fenton reactions has been computed in aqueous solution involving  $\text{Fe}^{3+}$ -oxalate complexes and hydrogen peroxide. Moreover, in this process, the irradiation of UV possesses a direct ability to decompose hydrogen peroxide molecules into ( $\cdot\text{OH}$ ) radicals. The drawback of Fe(III) species accumulation throughout the conventional Fenton process has been avoided in the photo-Fenton process due to the advantage of regenerating Fe(II) ions that catalyze Fenton's reaction (Eq. 1) and, consequently, to provide additional amounts of hydroxyl radicals [1, 29].

Several researchers studied the ability of the AOPs in wastewater treatment [24-26]. *Silva et al.*, 2015 examined the integration ability of photo-Fenton and flotation technologies in wastewater treatment [34-37]. *Deshpande et al.* (2019) conducted Fenton and UV/ $\text{H}_2\text{O}_2$  processes to eliminate 4-hydroxybenzoic acid from wastewater. This study proved that the most desirable condition for pollutant degradation is acidic pH [25]. Another study done by the same team of *Deshpande et al.* used AOPs namely UV/ $\text{H}_2\text{O}_2$ , UV and dark Fenton, and solar-Fenton to eliminate 4-Nitrobenzoic acid benzoic acid from wastewater. They have proved that the photo-Fenton process with the condition of acidic pH was more effective in wastewater treatment compared to other oxidation processes [26]. *Perez et al.* (2002) proved the highly effective combination of Fenton, Fenton-like, and photo-Fenton processes in textile wastewater treatment under the conditions of temperature, light intensity, pH, and the initial dosage of hydrogen peroxide and iron ions [38]. Other previous studies have conducted the Fenton process to treat polluted water using green Ferric nanoparticles produced from celery leaves [44], zerovalent iron nanoparticles produced from ficus leaves [45], and celery leaves [46].

According to the literature, there is no previous work

has investigated the ability of the photo-Fenton method in the treatment of wastewater discharged from Al-Samawa refinery plant. This research aims to study this case by using the photo-Fenton technology under specific operating variables in the first part. Then, the impact of varying the solution temperature on the removal efficiency under the desired operating parameters was studied. Furthermore, kinetic research on the effect of pH and  $\text{H}_2\text{O}_2$  concentration was conducted. In the second part, a comparative investigation of the treatability among UV-photolysis, Fenton, and photo-Fenton processes have been conducted and this comparison has not been done before for the present case study.

## EXPERIMENTAL SECTION

### Chemical and analytical Analysis

The refinery wastewater specifications obtained from the Al-Samawa refinery plant/ South of Iraq are presented in Table 1. Hydrogen peroxide (Germany 45 percent wt/wt.), NaOH (Thomas Baker), ferrous sulfate (Thomas Baker), and  $\text{H}_2\text{SO}_4$  (SDFCL 98 percent purity) were utilized. At the end of each experiment, the treated samples were prepared and determined using a UV-1800 spectrophotometer (Shimadzu Inc., Japan). The WTW pH-720 meter has been utilized to determine the pH and conductivity measurements.

The organic removal efficiency was estimated using Eq. (12):

$$Y_{\text{OCRE}} = \frac{B_0 - B_t}{B_0} \times 100\% \quad (12)$$

Where:

$Y_{\text{OCRE}}$  = the percent of organic removal;

$B_0$  = Initial concentration before treatment ( mg/L), and

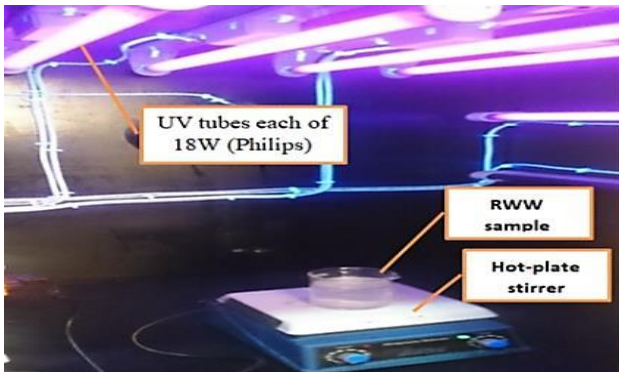
$B_t$  = Organic concentration after treatment (mg/L).

### Photo-Fenton batch reactor

Experiments on advanced oxidation were conducted in a 250 ml glass batch reactor mounted above a magnetic stirring in a UV chamber equipped with six 18W UV tubes. The tubes (Philips) have a wavelength of 365 nm (Fig. 1). Every run comprised 150 mL of RWW solution and was evaluated concerning the operational factors detailed in Table 2. A magnetic stirrer (DAIHAN LABTECH; Korea; LMS1003; 60-1500 rpm) was employed to mix RWW at a 200 rpm steady agitation rate. The pH of the solution was adjusted to the desired level using diluted  $\text{H}_2\text{SO}_4$  or NaOH.

**Table 2: Operational parameters**

Variables	Ranges
X <sub>1</sub> : Reaction time (min.)	30-90
X <sub>2</sub> : Hydrogen peroxide (ppm)	25–250
X <sub>3</sub> : pH	2–8.5

**Fig.1: Photo-Fenton reactor**

### Experimental Design

Several steps are included in the Response Surface Methodology (RSM), Such as the Design of Experimental (DOE) which is classified as a test on input variables to create and examine the adequacy of the response surface model [12,13,18]. The surface model is beneficial for predicting probable responses that could occur as a result of the change in the ranges of the operating variables. In the final step, the adequacy of the obtained model is checked using the ANOVA test [7, 9].

In the present study, Response Surface Methodology/ type Factorial design and Minitab (a statistical application), were employed to construct the treatment experiments and assess the findings produced under the influence of the operational parameters (Table 2). The factorial statistical approach was used to conduct a total of 30 experiments.

### RESULTS AND DISCUSSION

Table 3 presents the operational variables and the studied responses of the final oil content and its removal efficiency for every run.

#### Mathematical correlation of the studied response

The mathematical equation (Eq. 13) in terms of real factors was established based on the experimental findings. This equation relates oil content response to the operating variables and demonstrates the interactions among these parameters.

**Table 3: Results of batch photo-Fenton oxidation experiments**

Run	X <sub>1</sub> : Reaction time (min)	X <sub>2</sub> : Hydrogen peroxide (ppm)	X <sub>3</sub> : pH	Oil content (ppm)	Y <sub>OCRE</sub> : Oil content removal (%)
1	90	250	8.5	28.61	52.72
2	30	250	2	39.00	35.54
3	30	25	8.5	45.71	24.45
4	90	25	2	26.08	56.89
5	60	50	3.5	17.96	70.32
6	60	100	5	18.01	70.24
7	30	150	6.5	26.37	56.41
8	60	200	6.5	16.95	71.99
9	30	200	3.5	21.80	63.97
10	60	150	2	21.68	64.17
11	30	100	2	33.83	44.08
12	90	50	8.5	28.61	52.72
13	90	150	3.5	9.78	83.83
14	90	100	6.5	11.46	81.06
15	90	200	5	27.28	54.91
16	60	25	6.5	27.89	53.90
17	60	250	3.5	26.45	56.29
18	60	200	8.5	27.73	54.17
19	60	150	5	11.64	80.76
20	30	100	8.5	۳۲,۹۱	45.60
21	60	50	2	19.52	67.74
22	30	250	6.5	25.29	58.20
23	30	25	3.5	34.30	43.30
24	90	25	5	22.92	62.12
25	90	50	6.5	18.87	68.81
26	90	100	3.5	4.32	92.87
27	90	200	2	22.27	63.20
28	90	150	8.5	21.99	63.64
29	90	250	5	27.32	54.84
30	30	50	5	19.98	66.98

$$\text{Oil content (ppm)} = 110 - 0.972 X_1 - 0.536 X_2 - 24.4 X_3 + 0.0052 X_1^2 + 0.0036 X_2^2 + 4.37 X_3^2 + 0.001 X_1 X_2 + 0.0165 X_1 X_3 - 0.0072 X_2 X_3 \quad (13)$$

#### Analysis of variance (ANOVA) test

The (ANOVA) test is a reliable method to assess the adequacy and importance of the proposed mathematical model [18]. The Significance of the Proposed Models is checked by regression coefficient, P-value, and F-value [13]. If the estimated p-value for each of the models is less than

**Table 3: ANOVA test results for the advanced oxidation process**

Effect	Sum of Squares	DF	Mean Squares	F-value	P-value
Regression	18130.17	12	1510.848	59.95827	< 0.001
Residual	453.57	18	25.198		
Total	18583.74	30			

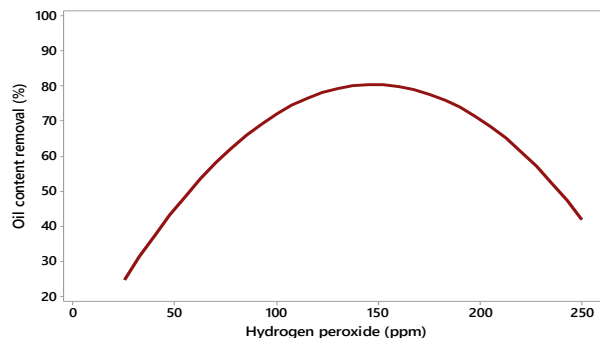
0.05, it indicates that the obtained model is significant [7, 8]. Table 3 demonstrates the analysis of variance (ANOVA) results for oil content, where the F-value was 59.96, and the Prob (P) value was less than 0.001 at 95% confidence level. These outcomes indicate that the proposed model is highly significant. Furthermore, this model is significant, as indicated by the high magnitude of the regression coefficient ( $R^2=0.83$ ) for oil content response.

#### Effect of $H_2O_2$ concentration

The relationship between the initial concentration of hydrogen peroxide and the oil content percentage of removal is demonstrated in Fig. 2. The  $H_2O_2$  molecules are directly decomposed by UV irradiation into  $\cdot OH$  radicals like the photolysis of  $H_2O_2$  process [33,37]. It was discovered that the removal effectiveness improved as the  $H_2O_2$  concentration rose from 25 to 100 ppm, peaking at 70 percent at 100 ppm of  $H_2O_2$ , 90 minutes of irradiation time, and ambient temperature. The removal effectiveness of the oil content shown in RWW was negatively impacted by the excessive addition of  $H_2O_2$  over 100 ppm. At 250 ppm of  $H_2O_2$ , the removal effectiveness was reduced to 54.3% because the  $\cdot OH$  free radical would react with the  $H_2O_2$  instead of the organic pollutants. In other words, it creates  $HO\cdot_2$ , which is not as reactive as  $\cdot OH$  as revealed in Eq. 5 where  $HO\cdot_2$  radicals are significantly less reactive with organic pollutants because they are categorized by a lower oxidization power [33]. The reaction reduced the effectiveness of the treatment. Moreover, if the  $H_2O_2$  dosage is low, the formation of free radicals will be less, then the treatment will be inefficient. The same results were stated by [25,29,40,41].

The mathematical correlation of oil content removal efficiency ( $Y_{OCRE}$ ) relating to the  $H_2O_2$  dosage at pH 7, 90 min irradiation time, and at room temperature is illustrated in Eq. (14).

$$Y_{OCRE} = -0.004X^2 + 1.09X \quad R^2 = 0.911 \quad (14)$$



**Fig. 2: Effect of hydrogen peroxide concentration on oil content removal; pH=7, irradiation time=90min, and at room temperature**

#### Effect of pH

Iron speciation,  $H_2O_2$  constancy, oxidant, and substrate actions, and all of these are regulated by pH. The effect of solution pH level on the removal of oil from RWW by photo-Fenton technology was examined in the current research under the pH range of 2 to 8.5, 90 min irradiation time, 100 ppm of  $H_2O_2$ , and at ambient temperature. The findings in Fig. 3 demonstrated that at approximately pH=3, the highest removal efficacy of 92.75 percent was reached.

As observed, when the pH value increased above this value, the organic removal efficiency minimized gradually until it reached 62.7% at pH=8.5. It is obvious that a significant removal efficiency was achieved when the solution was more acidic, but it should not be less than the optimal value due to the stability of hydrogen peroxide which reduced the reactivity between Fe ions and  $H_2O_2$  [29,37]. However, the removal tends to minimize when the solution pH increases toward the basic status due to the minimizing of the oxidation potential of  $\cdot OH$  radicals as a result of settling down the iron oxy-hydroxides formed via the process. Eq. 4 relates the oil content removal efficiency ( $Y_{OCRE}$ ) to the solution pH at 100 ppm  $H_2O_2$ , irradiation time of 90 min, and ambient temperature. Similar results were stated by [25, 26].

Equation 15 relates the oil content removal efficiency ( $Y_{OCRE}$ ) to the solution pH at 100 ppm of  $H_2O_2$ , 90min of irradiation time, and at room temperature:

$$Y_{OCRE} = -2.659 X^2 + 27.89 X \quad R^2 = 0.951 \quad (15)$$

#### Effect of irradiation time

The analysis of the photo-Fenton treatment's irradiation time variable and its impact on the effectiveness

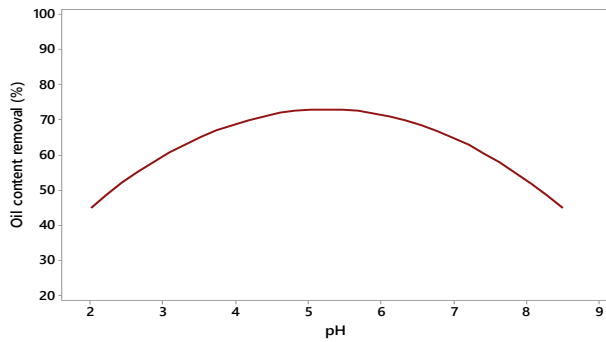


Fig. 3: Effect of solution pH on oil content removal; hydrogen peroxide concentration = 100 ppm, irradiation time = 90 min, and at room temperature

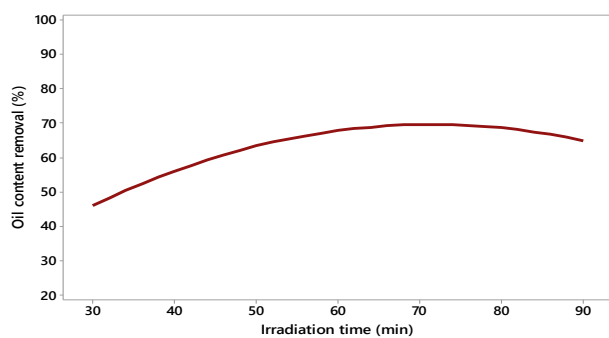


Fig. 4: Effect of irradiation time on oil content removal; hydrogen peroxide concentration = 100 ppm, pH = 7, and at room temperature

of removing oil content was performed. The pH value and  $H_2O_2$  concentration were set at 7 and 100 ppm, respectively, at room temperature for this experiment. Fig. 4 demonstrates the relationship between the irradiation time and oil content removal effectiveness during the treatment. Experiments were carried out to identify the best time of the photo-Fenton effectiveness in organic percent removal. The elimination effectiveness rose when the irradiation time was increased. This behavior with irradiation time can be interpreted by considering that the Fenton reaction, which is accomplished within a few seconds, benefits from a higher load of Fe(II) ions, while unfavorable reactions like (1) and (5), because of the low amount of hydroxyl radicals, require more irradiation time to manifest, and their impacts appear only for long irradiation times when they contest with slower CAOPs reactions. The result agreed with [29,33,38,42].

Equation 16 explains the relation between the removal efficiency of oil content ( $Y_{OCRE}$ ) and the time of irradiation at 100 ppm of  $H_2O_2$ , pH 7, and ambient temperature:

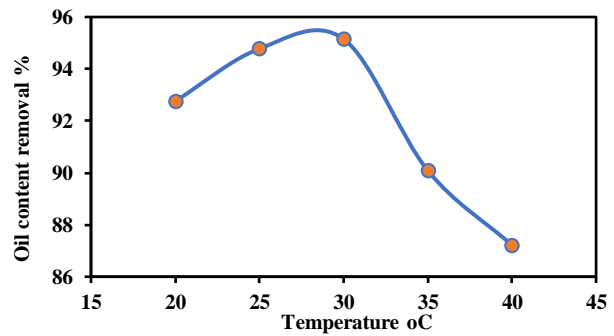


Fig. 5: Effect of temperature on oil content removal efficiency; hydrogen peroxide concentration = 100ppm, pH = 3, irradiation time = 90 min

$$Y_{OCRE} = -0.014 X^2 + 1.95 X \quad R^2 = 0.963 \quad (16)$$

#### Effect of temperature

The reaction temperature is a key parameter that impacts the treatment process [38]. Fig. 5 depicts the impact of temperature variation on RWW oil removal efficiency. When the temperature changed from 20 to 30°C, the removal efficiency improved from 92.75 percent to 95.20 percent. At 40°C, the treatability was down to 87.2%. Excessive temperature rise speeds up the breakdown of hydrogen peroxide into oxygen and water, reducing the generation of free radicals and reducing the effectiveness of oil-degrading deterioration due to oil content. As observed, the higher value of oil content removal efficiency was at 30°C, but when the temperature increased above this value, the removal efficiency decreased rapidly. So, it is obvious that temperature markedly impacts the degree of oil content removal because the temperature could be in assisting the dissolution of hydrogen peroxide, the formation of hydroxyl radicals, or the recovery of Fe(II) ions [38,43]

The mathematical correlation between the removal efficiency of oil content ( $Y_{OCRE}$ ) and the temperature at 100 ppm of  $H_2O_2$ , pH 3, and 90 min of irradiation is (Eq. (17)):

$$Y_{OCRE} = -0.273 X^2 + 8.976 X \quad R^2 = 0.958 \quad (17)$$

#### Kinetic study

As mentioned before photo-Fenton is conducted by the simultaneous action of the Fenton system together with UV irradiation which increases the contribution of the radical pathway in the photo-Fenton process due to



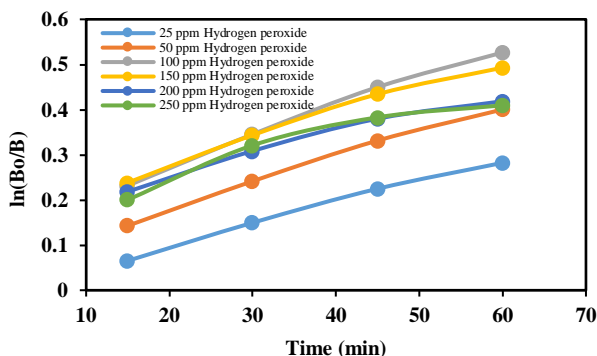


Fig. 6: Pseudo first-order model for oil content degradation against the irradiation time in the case of hydrogen peroxide experiments at pH =7, and 30 °C

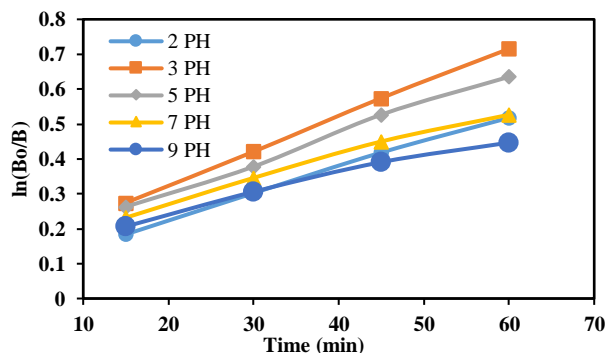


Fig. 8: Pseudo first-order model for oil content degradation against the irradiation time in the case of pH experiments at hydrogen peroxide concentration = 100 ppm at 30 °C

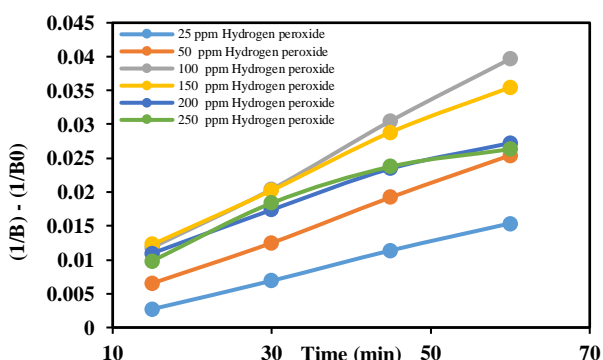


Fig. 7: Pseudo second-order model for oil content degradation against the irradiation time in the case of hydrogen peroxide experiments at pH =7, and 30 °C

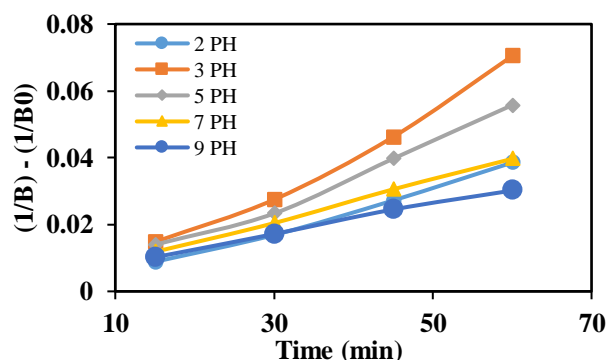


Fig. 9: Pseudo second order model for oil content degradation against the irradiation time in the case of pH experiments at hydrogen peroxide concentration = 100 ppm at 30 °C

an additional generation of hydroxyl radicals. Thus, it can be concluded that the active hydroxyl radicals are formed through three possible sources: the original  $\text{Fe(II)/H}_2\text{O}_2$  reaction, photolysis of  $\text{H}_2\text{O}_2$ , and  $\text{Fe(II)}$  sensitization. A competition kinetics study was performed to estimate the pseudo-first and second-order rate constants for the reactions of the pollutants with hydroxyl radicals depending on the values of pH and hydrogen peroxide. These models are illustrated in Fig. 6 to Fig. 9. Six tests at various  $\text{H}_2\text{O}_2$  concentrations of 25, 50, 100, 150, 200, and 250 ppm were performed to analyze the effects of hydrogen peroxide concentration on the kinetic constants. According to Eqs (2) and (3), the values of the rate constants,  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{L}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ ), have been calculated. Fig. 6 displays the values of  $\ln(B_0/B)$  about the normalized irradiation time. The  $1/Ct$  vs. normalized irradiation time is shown in Fig. 7.

Other studies were carried out at various pH values of 2, 3, 5, 7, and 9 at 100 ppm of hydrogen peroxide concentration and

30°C to explore the impact of pH value on the effectiveness of organic removal. The linearized form of the two models is shown clearly in Figs .8 and 9. Tables 4 and 5 provide the values of rate constants obtained from the two studied models. The significance indication of each value of rate constants was characterized depending on the regression coefficient ( $R^2$ ) value. The higher value of  $R^2$  indicates the best model obtained.

Tables 4 and 5 demonstrate that for  $\text{H}_2\text{O}_2$  experiments, the pseudo-second-order model matched the data. However, the pseudo-first-order model suited pH experiments which is similar to that stated by [29,39].

#### Adsorption isotherms

The equilibrium isotherms of adsorption have been studied to find which isotherm model is more fitted for this process than others. The most models investigated in literature are Langmuir, Freundlich, and Temkin isotherms models [2,6,20]. Fig. 10 (a, b, and c) shows the core findings of

**Table 4: Rate constants of hydrogen peroxide experiments**

H <sub>2</sub> O <sub>2</sub> Concentration (ppm)	First order		Second order	
	k <sub>1</sub> (L/min)	R <sup>2</sup>	k <sub>2</sub> (L/mg.min)	R <sup>2</sup>
25	0.0048	0.9931	0.0003	0.9995
50	0.0058	0.9938	0.0004	0.9950
100	0.0066	0.9926	0.0006	0.9991
150	0.0057	0.9849	0.0005	0.9973
200	0.0045	0.9710	0.0004	0.9870
250	0.0046	0.9139	0.0004	0.9440

**Table 5: Rate constants of pH experiments**

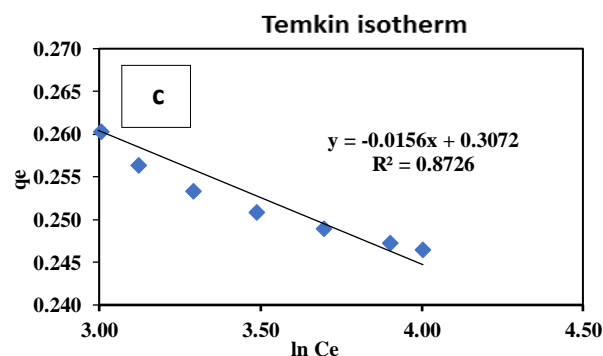
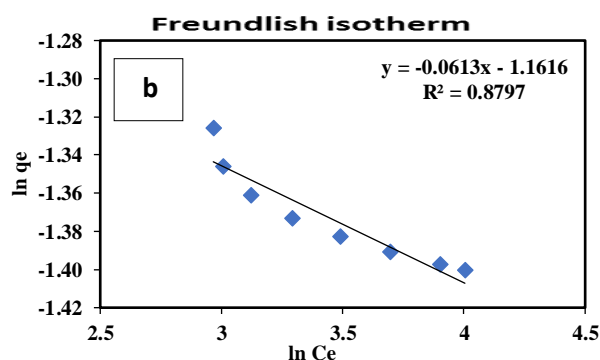
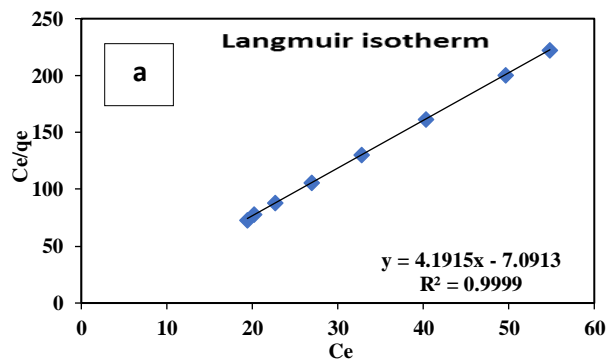
pH value	First order		Second order	
	k <sub>1</sub> (L/min)	R <sup>2</sup>	k <sub>2</sub> (L/mg.min)	R <sup>2</sup>
2	0.0075	0.9984	0.0007	0.9943
3	0.0098	0.9998	0.0012	0.9810
5	0.0084	0.9964	0.0009	0.9863
7	0.0066	0.9926	0.0006	0.9991
9	0.0054	0.9853	0.0004	0.9972

isotherms investigation. These results revealed that Langmuir model was more fitted ( $R^2 = 0.9999$ ) for photo-Fenton elimination of oil content than other isotherm models.

#### A comparison among oxidation methods

For comparison, three experiments were conducted involving UV-photolysis (pH 6.86 and exclusive use of UV irradiation), Fenton reaction (ferrous sulfate and hydrogen peroxide, pH 3 without UV irradiation), and photo-Fenton process (hydrogen peroxide and ferrous sulfate with UV irradiation and pH 3).

The findings of these experiments revealed that the UV-photolysis was not relatively sufficient to remove oil content efficiently due to the lower molar absorption coefficient of H<sub>2</sub>O<sub>2</sub> in the UV region which means that a rather strong amount of H<sub>2</sub>O<sub>2</sub> provides an efficient oxidation process of the oil content [29]. The removal efficiency of oil content attained 49.2% using the UV-photolysis technology at the end of the total irradiation time of 3 h. The second time, when the Fenton method was used, the removal effectiveness was 69.6% after 1.5 h of treatment time. This expected value is the result of the reaction between ferrous ions and hydrogen peroxide, which forms free radicals. It's important to note that hydrogen peroxide and iron ions serve as the process'



**Fig. 10: Adsorption equilibrium isotherms: (a) Langmuir, (b) Freundlich, and (c) Temkin**

Fenton limiting reagent. The inferior is responsible for the free radicals where the rate of oxidation is enhanced with the irradiation of UV which is absent in the Fenton process [38].

However, better outcomes are obtained using iron reagents in conjunction with UV radiation. The photo-Fenton technique was more treatable, attaining 92.75 percent of elimination efficacy in a similar irradiation time. According to the present observation, the integration of UV radiation with Fe(II) or Fe(III) improves the rate of degradation of the oil content [29]. As a core finding, the efficient technology in refinery wastewater treatment was photo Fenton compared to other oxidation processes studied.



## CONCLUSIONS

The photo-Fenton (UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>) treatment technology is extremely active for higher oil content removal from refinery wastewater. The optimum values of the operational variables are (90 min., 100 ppm of H<sub>2</sub>O<sub>2</sub>, and pH 3). The impact of solution temperature in the range of 20–400 °C on the removal efficiency was studied. It revealed that the temperature notably influences this treatment process, where the highest removal of organic content (95.15%) was achieved at 30°C. The Langmuir model was a more fitted model ( $R^2 = 0.9999$ ) for photo-Fenton elimination of oil content than Freundlich and Temkin isotherm models. The pseudo-second-order model was more suited for H<sub>2</sub>O<sub>2</sub> trials. However, in pH studies, the pseudo-first-order model fits better. Finally, a comparative investigation of the treatability among UV-photolysis (UV/H<sub>2</sub>O<sub>2</sub>), Fenton (H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>), and photo-Fenton (UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>) processes has been done. The results of this comparison revealed that the photo-Fenton process possesses the highest removal efficiency of pollutants (92.75%) compared to those of the UV-photolysis process (49.2%) and the Fenton process (69.6%). Based on the core results obtained from this work, photo-Fenton technology is extremely effective for refinery wastewater treatment.

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