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Batch and Continuous Photo-Fenton Oxidation of Reactive-Red Dye from Wastewater

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ABSTRACT

This paper aims to investigate the ability of photo-Fenton technology to remove Reactive Red dye (RR-dye) from wastewater using batch and continuous operating modes. The batch mode of photo-Fenton removal of organic content was conducted under the influence of solution pH (3–10), hydrogen peroxide (25–100 ppm), irradiation time (20–90 min), ferrous sulphate (5–20 ppm), and temperature (25–60 °C). For comparison, the continuous treatment was conducted under the influence of the flow rate of the contaminated solution (10, 20, 30, 40, and 50 mL/min). The results revealed that the treatability of the batch mode was more effective compared to the continuous mode. In the batch process, the organic contaminant was completely removed compared to that of 82% obtained when the continuous system was performed. The optimization process showed that the optimal values of the operating variables in the case of the batch removal of RR-dye were 3, 78 ppm, 90 min, 20 ppm, and 60 °C for pH, hydrogen peroxide, irradiation time, ferrous sulphate, and temperature, respectively. Moreover, the reversion F-value was 21.69, the probability P value was less than 0.001, and the correlation coefficient was (R^2 = 0.9455), which illustrative the significance of the model obtained for the batch process.

Keywords: dyes, wastewater treatment, advanced oxidation processes, central composite design, optimization.

INTRODUCTION

A huge amount of wastewaters was annually discharged from domestics and industries activities to the environment. These wastewaters contain numerous pollutants such as heavy metals, oil contents, high salinity, dyes, etc. (AlJaberi et al. 2020a). Dyes are significant toxic contaminants that affect human and aquatic systems and, consequently, the ecological requirements due to their significant solubility. Wastewater containing dyes is continually discharged from several activities such as textile and coloring industries. Synthetic dyes are classified as toxic water contaminants that are also oncogenic (AlJaberi et al. 2020a, Hassaan et al. 2017). The complex aromatic construction and the relative stability of these colors complicate the mission of wastewater treatment methods. Consequently, they will affect the ability of treatment methods. Thereby, the produced wastewater will extensively impact the environment (Hassan and Naeem 2019, AlJaberi et al. 2020b, AlJaberi et al. 2020c). Lime methods are predictable to eliminate pollutants that may cause ecological problems, and they are tremendously useful to energy well-organized, a cost-effective, eco-benign, and lime alternative (Hassan and Al-Zobai 2019). Physical and chemical methods have stilled been employed for the treatment of dye wastes (Hadi et al. 2021).

As observed in the literature, not all of these treatment methods are completely effective in wastewater treatment. An additional effective treatment method is the advanced oxidation processes (AOPs) (Atiyah et al. 2020). AOPs are fundamentally physicochemical processes in nature that generate almost oxidizing species, mainly free radical (•OH) consume the highest oxidation potential subsequent the fluorine radicals (Diya'uddeen et al. 2011, AlJaberi 2018). This treatment process can convert organic pollutants into inoffensive inorganic compounds.

Photo-Fenton treatment method is an integration process containing Fenton part using ferrous sulphate and hydrogen peroxide and UV part that generates free radical (Diya'uddeen et al. 2015) as explained in Eq. (1):

$$FE^{2+} + H_2O_2 \rightarrow FE^{3+} + HO^- + HO^\bullet \quad (1)$$

Hydrogen peroxide (H_2O_2) has almost performed as an initiator in the advanced oxidation processes. It can increase the generation rate of free radicals depending on the reaction that occurred between ozone and its conjugate base. Consequently, the considerable advantage of AOPs involving H_2O_2 has recently increased aimed at the active oxidation of toxic contaminants present in wastewater. Several studies concerned the elimination of organic contaminants from wastewater using AOPs such as photo-Fenton oxidation (Ebrahiem 2017), solar photo-two catalyst ZnO and TiO_2, and others to remove oil, mineralization, gasoline-contaminated waters, and olive mill effluent (AlJaberi et al. 2020b, Aziz and Daud 2012, Chatzisymeon et al. 2013).

This work aims to remove reactive red from synthetic wastewater performing photo-Fenton oxidation processes using batch operating mode then a continuous operating mode. At first, the batch reactor has employed to investigate the effects of the operating variables (pH, H_2O_2, irradiation time, iron (Fe^{+2}), and temperature) on the treatment efficiency. Then, the continuous process has performed to find the influence of the flow rate on the ability of the photo-Fenton oxidation process to remove pollutants from wastewater.

EXPERIMENTAL WORK

Chemicals and analytical analysis

All chemicals performed in this work are of analytical grade and they had used without any additional purification. They are reactive red dye (RR-dye) (Figure 1) with a maximum absorption wavelength (540 nm), hydrogen peroxide (45 wt.%), ferrous sulphate (99% purity), and sodium hydroxide (Thomas baker). The stock solution was prepared using distillate water.

The RR-dye concentration of the treated solution was determined by using a UV-1800 spectrophotometer (Shimadzu Inc., Japan). The pH values were measured using WTW pH-720 meter, where the pH value of the solution was adjusted using a dilute H_2SO_4 or NaOH.

The dye removal efficiency was obtained using Eq. (2):

$$Y = \frac{C_\circ - C_t}{C_\circ} \times 100\% \quad (2)$$

where: Y – is the percentage of dye removal; C_o, initial concentration before the decolorization process (mg dye/L), and C_t – is the organic concentration after the treatment process (mg dye/L).

Photo-Fenton using a batch reactor

The experiments of the photo-Fenton were carried out using a chamber that was made totally of wood with a dimension of 60x60x60 cm^3 and coated with black color. A glass reactor of 250 mL was used for batch experiments and placed on a magnetic stirrer (250–1250 rpm) to provide a constant stirring speed of 250 rpm (Figure 2). This system was placed in a UV chamber armed with two UV tubes, each of 6W (Philips) having a wavelength of 365 nm. After

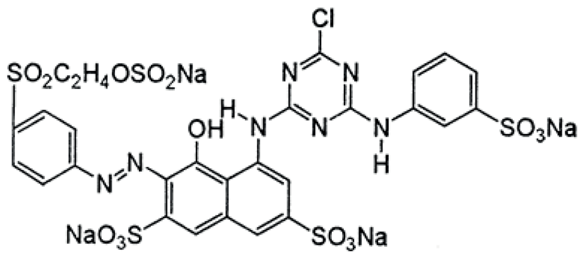

Figure 1. The chemical structure of the reactive red (RR)

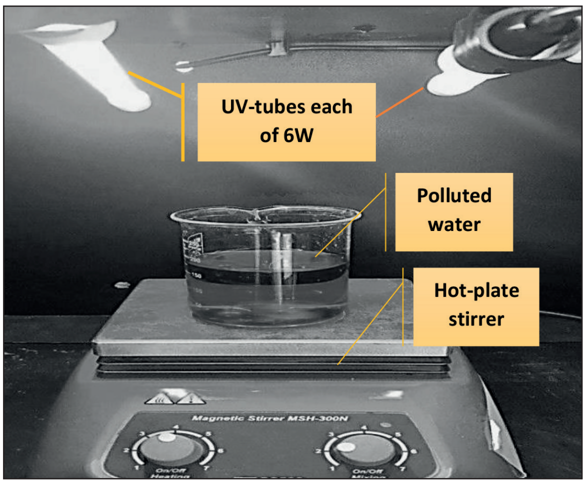

Figure 2. The batch system of the photo-Fenton process

25 min, the solution was separated and analyzed using a UV–VIS Spectrophotometer to estimate the final RR concentrations.

Then a comparison was done with a continuous system of the photo-Fenton oxidation process using different values of the flow rate that ranges from 10 mL/min to 50 mL/min.

Experimental design

Response Surface Methodology type central composite design (RSM-CCD) method and a statistical software program (Minitab) were used to design the experiments for the batch part of the present study, found the impacts of the operating variables, analyzed the results, and estimate the optimal conditions. The influence of the operating variables, pH (X_1), hydrogen peroxide (X_2), irradiation time (X_3), Ferrous sulphate (X_4), and Temperature (X_5), had been investigated according to their ranges explained in Table 1. The real and coded values of the operational variables have listed in Table 2, where the rotability is 2. A total of 46 experiments had done according to the RSM-CCD method.

Table 1. Operational parameters

Parameters	Ranges
X_1: pH	3-10
X_2: H_2O_2 concentration (ppm)	25-100
X_3: Irradiation time (min)	20-90
X_4 :Ferrous sulphate (ppm)	5-20
X_5: Temperature (°C)	25-60

The mathematical correlation between the response and the operational variables could be achieved according to the equation (3) (AlJaberi et al. 2020b):

$$Y = B_0 + \sum_{i=1}^{q} B_i X_i + \sum_{i=1}^{q} B_{ii} X_i^2 + + \sum_{i}\sum_{j} B_{ij} X_i X_j + \varepsilon \quad (3)$$

where: X_1, X_2, to Xq – denote the operational variables; B_o, B_i, to B_{ij} – are called the regression coefficients, and Y – is the studied response.

Table 2. Natural and coded working variables

Natural variable (Xi)	Coded variables				
	-2	-1	0	1	2
X_1: pH	3	4.5	6.5	8.5	10
X_2: H_2O_2 concentration (ppm)	25	45	62.5	82.5	100
X_3 : Irradiation time (min.)	20	35	55	75	90
X_4 : Ferrous sulphate (ppm)	5	7.5	12.5	17.5	20
X_5: Temperature (°C)	25	35	42.5	52.5	60

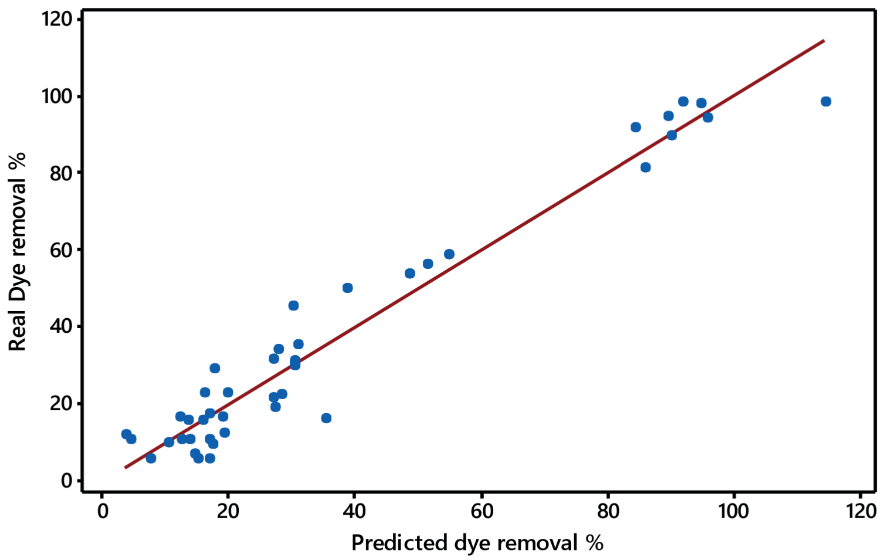

Figure 3. Real RR-dye removal response vs. predicted response values

Table 3. Results of the studied variables

Run	X_1: pH	X_2:H_2O_2 (ppm)	X_3: Time (min)	X_4: Fe(II) (ppm)	X_5: Temp. (°C)	Dye removal %
1	6	25	20	12.5	42.5	5.44
2	6	25	90	12.5	42.5	6.69
3	6	100	20	12.5	42.5	9.81
4	6	100	90	12.5	42.5	22.31
5	3	62.5	55	5	42.5	94.81
6	3	62.5	55	20	42.5	98.44
7	10	62.5	55	5	42.5	10.44
8	10	62.5	55	20	42.5	16.06
9	6	25	55	12.5	25	15.44
10	6	100	55	12.5	25	34.19
11	6	25	55	12.5	60	5.44
12	6	100	55	12.5	60	12.31
13	6	62.5	20	5	42.5	16.69
14	6	62.5	90	5	42.5	22.94
15	6	62.5	20	20	42.5	21.69
16	6	62.5	90	20	42.5	58.56
17	3	62.5	55	12.5	25	94.19
18	10	62.5	55	12.5	25	10.44
19	3	62.5	55	12.5	60	98.56
20	10	62.5	55	12.5	60	15.44
21	6	25	55	5	42.5	17.31
22	6	100	55	5	42.5	5.44
23	6	25	55	20	42.5	45.43
24	6	100	55	20	42.5	53.56
25	3	62.5	20	12.5	42.5	91.69
26	3	62.5	90	12.5	42.5	97.94
27	10	62.5	20	12.5	42.5	10.44
28	10	62.5	90	12.5	42.5	22.94
29	6	62.5	55	5	25	35.44
30	6	62.5	55	20	25	49.81
31	6	62.5	55	5	60	10.44
32	6	62.5	55	20	60	56.06
33	6	62.5	20	12.5	25	9.19
34	6	62.5	90	12.5	25	19.19
35	6	62.5	20	12.5	60	16.69
36	6	62.5	90	12.5	60	31.69
37	3	25	55	12.5	42.5	81.06
38	3	100	55	12.5	42.5	89.81
39	10	25	55	12.5	42.5	11.69
40	10	100	55	12.5	42.5	29.19
41	6	62.5	55	12.5	42.5	31.06
42	6	62.5	55	12.5	42.5	30.44
43	6	62.5	55	12.5	42.5	29.81
44	6	62.5	55	12.5	42.5	30.19
45	6	62.5	55	12.5	42.5	30.75
46	6	62.5	55	12.5	42.5	29.94

RESULTS AND DISCUSSION

Batch photo-Fenton oxidation process

Table 3 listed the obtained results of the experimental values of RR-dye removal efficacy in the case of the batch-photo-Fenton oxidation process. The observed dye removal values vary between 5.43 to 98.56%, which is in good agreement with its predicted values as shown in Figure 3.

The regression model

Based on the findings listed in Table 3, the regression equation (Eq. (4)) was developed in terms of real factors explaining the interaction between the operating variables to the dye removal efficiency:

$$\text{Dye removal \%} = 215.3 - 48.45 X_1 + 0.597 X_2 + 0.143 X_3 - 5.99 X_4 + 0.01 X_5 + 2.734 X_1^2 - 0.00597 X_2^2 - 0.00558 X_3^2 + 0.0996 X_4^2 - 0.0085 X_5^2 + 0.0189 X_1 X_2 + 0.0107 X_1 X_3 - 0.031 X_1 X_4 + 0.0110 X_1 X_5 + 0.00214 X_2 X_3 + 0.0178 X_2 X_4 - 0.00453 X_2 X_5 + 0.0292 X_3 X_4 + 0.00204 X_3 X_5 + 0.0595 X_4 X_5 \quad (4)$$

The analysis of variance (ANOVA) test, as listed its results in Table 4, proved that the model obtained is significant because the p-value was less than 0.001 and the F-value equals (21.69). Considering these results and the high values of the regression coefficient ($R^2 = 0.9455$) and adjusted ($R^2 = 0.9019$), it could be concluded that this model revealed the effectiveness status of the photo-Fenton process, and it could be used to remove RR dye from wastewater.

Thereby, the correlation of RR-dye removal efficiency will be as follows (Eq. (5)) after omitting effects that possess (P-Value) larger than 0.05 (interactions among variables-Bolded values in Table 4):

$$\text{Dye removal \%} = 215.3 - 48.45 X_1 + 0.597 X_2 + 0.143 X_3 - 5.99 X_4 + 0.01 X_5 + 2.734 X_1^2 - 0.00597 X_2^2 - 0.00558 X_3^2 + 0.0996 X_4^2 - 0.0085 X_5^2 \quad (5)$$

Effect of pH

The value of pH is extremely affecting the oxidation potential of free radicals. Moreover, the inorganic carbon concentration and the hydrolytic speciation of iron ions are powerfully affected depending on the pH value. Therefore, the pH impact in the photo-Fenton oxidation process should be strong-considered. The pH value affects the formation of free radicals and therefore, the efficacy of the oxidation process. At pH values over 6, the degradation process reduces since iron tends to precipitate by way of hydroxide derivative, decreasing the iron ions obtainability and the radiation transmission. The incompetent removal of pollutants at a pH value larger than 3 is due to the auto-decomposition of hydrogen peroxide (Davarnejad et al. 2014). Figure 4 reveals the inverse relation between the removal response and the solution pH throughout the use of the photo-Fenton treatment.

As shown that the highest RR-dye removal efficiency (93.2%) was obtained at pH 3 using the system of the batch- UV/ H_2O_2/ Fe^{2+} after 90 min of the irradiation time. While it reached 24.7% at pH = 6 within the same irradiation time of 90 min. Therefore, at higher values of the solution pH, iron ions precipitate as hydroxide and that will minimize the transmission of the irradiation (Ebrahiem et al. 2017).

Effect of H_2O_2

The oxidizing reagent using hydrogen peroxide is an essential parameter to accelerate the

Table 4. ANOVA test results for the photo Fenton process

Source	DF	Sum of Squares	Mean Squares	F-value	P-value
Model	20	38253.7	1912.7	21.69	< 0.001
Linear	5	27024.0	5404.8	61.30	< 0.001
Square	5	13952.6	2790.5	31.65	< 0.001
2-Way interaction	10	688.2	68.8	0.78	**0.647**
Error	25	2204.1	88.2		
Lack-of-Fit	20	2203.0	110.1	476.36	< 0.001
Pure error	5	1.2	0.2		
Total	45	40457.8			

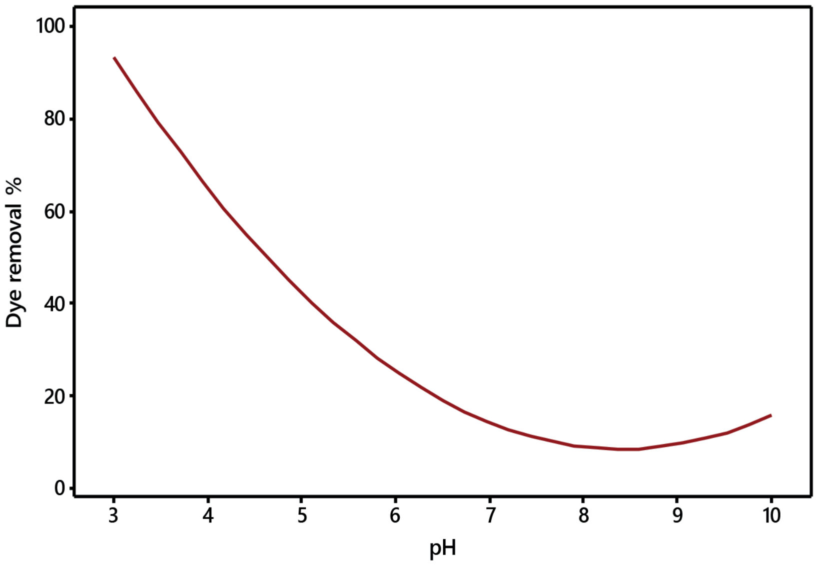

Figure 4. The influence of pH on RR-dye removal

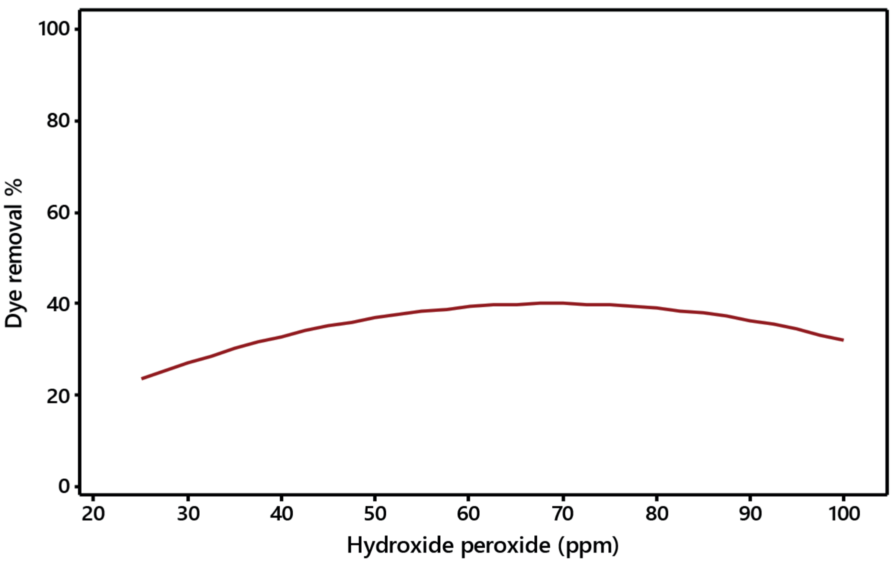

Figure 5. The influence of H_2O_2 on RR-dye removal

process of RR-dye removal. Designed values of H_2O_2 were added to the wastewater and then exposed to UV irradiation. Figure 5 explains the effect of adding different concentrations ranging from 25 to 100 ppm of hydrogen peroxide on the RR-dye removal efficiency.

As shown in Figure 5, the removal response attained a maximum efficiency of 42% at 78 ppm of H_2O_2 after 90 min of irradiation time. The reaction rate was dramatically increased when a value of H_2O_2 was added to the RR-dye solution then exposed to UV irradiation. The excessive adding of H_2O_2 more than 78 ppm impacts dye removal efficiency. When 100 ppm of hydrogen peroxide was added, 31% of the removal response was attained. So, a balance should be maintained of selecting the concentration required of hydrogen peroxide to achieve the higher elimination of pollutants. These core findings are agreed with that found by (Haji et al. 2011).

Effect of irradiation time

The irradiation time required for an efficient photo-Fenton process is necessary to remain as short as possible. Figure 6 shows that the removal efficiency of RR-dye with the increase of the irradiation time. The best removal efficiency was achieved at the optimum value of irradiation time. The increment of removal efficiency is related to the chemical oxidation of organic by the effect of free radicals. Several studies have stated that the

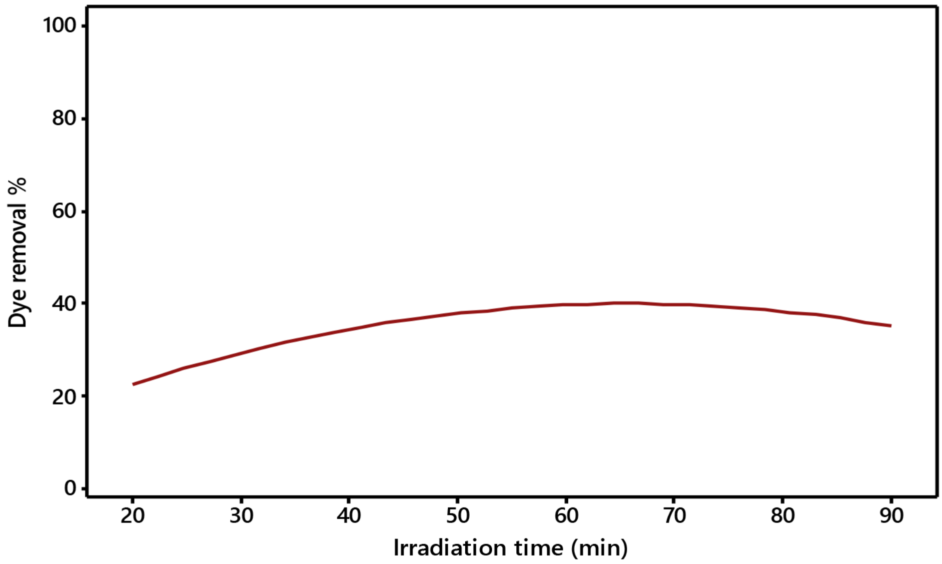

Figure 6. The influence of treatment time on the RR-dye removal

upsurge of irradiation time raises the efficiency of the photo-Fenton process as that found by (Davarnejad et al. 2014).

Effect of ferrous sulphate concentration

The best concentration of ferrous sulphate required to achieve a considerable elimination of the RR-dye from wastewater was investigated. The concentration of ferrous sulphate ranging from 5 to 20 ppm was studied. As observed in Figure 7, a 20 mg/L concentration of Fe^{2+} was the finest to obtain 48% of removal efficiency after approximately 90 min of irradiation time (Chatzisymeon et al. 2013).

Effect of temperature

Figure 8 demonstrates the variation of RR-dye removal efficiency against the raising of temperature from 25 to 60 °C. When the temperature raised from 20 to 45 °C, the removal efficiency increased from 30% to 38% and then decreased to 29.2 % at 60 °C. The upsurge in the temperature value has accelerated the decomposition of hydrogen peroxide that will be lessening the formation of free radicals and, consequently, minimized the elimination efficiency as stated by (Atiyah et al. 2020). As found, a positive influence was provided with temperature raising, within the designed range. The excessive raising of temperatures will

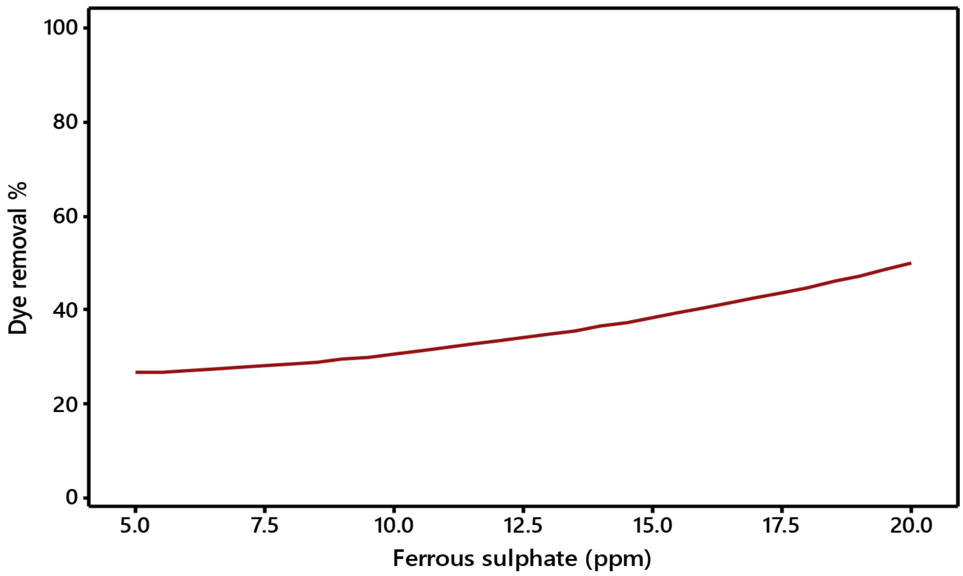

Figure 7. The influence of FeO_4S on the RR-dye removal

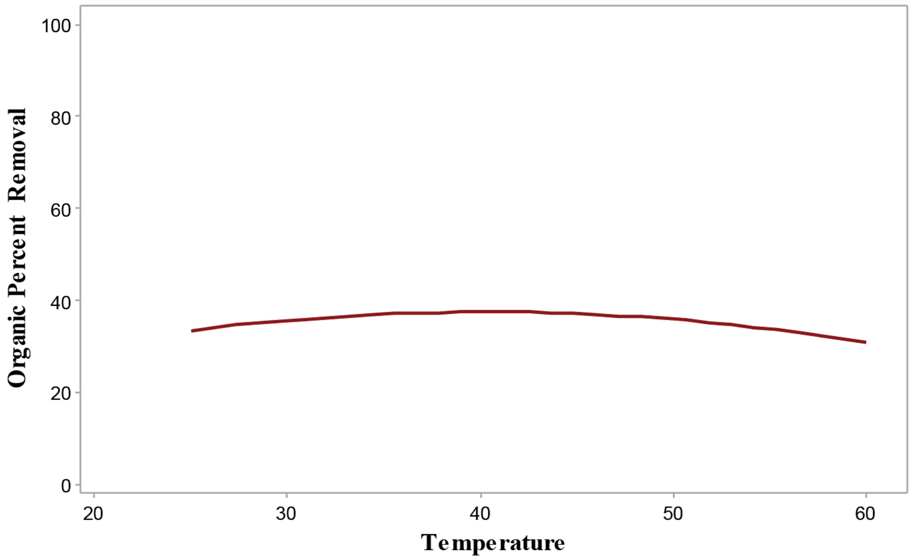

Figure 8. The influence of temperature on the RR-dye removal

Table 5. Correlations between RR-dye removal response and operating variables

Variables	Mathematical correlations
X_1: pH	$Y= 213.1- 48.6\ X_1 + 2.887\ X_1^2$
X_2: H_2O_2 concentration (ppm)	$Y= -0.45 + 1.17\ X_2 – 0.009\ X_2^2$
X_3: Irradiation time (min.)	$Y= 4.25 + 1.088\ X_3 – 0.008\ X_3^2$
X_4: Ferrous sulphate (ppm)	$Y= 26.38 – 0.31\ X_4 + 0.074\ X_4^2$
X_5: Temperature (°C)	$Y= 9.61 + 1.384\ X_5 – 0.017\ X_5^2$

cause vaporization of solution and chang the concentration of bio-contaminants; therefore, this temperature can be accurate as of the best temperature in the treatment conditions.

Table 5 listed the mathematical relation between the removal response with each variable in the case of mean values of other variables:

Optimization of the Operational Variables

The optimal values of the studied operating parameters were attained using Minitab-17 program. The core findings of the D-optimization measurement are shown in Figure 9 where the composite desirability equals 1. They show that complete dye removal could be achieved under these conditions of operating variables.

Continuous mode of the photo-Fenton process

Another assessment of the ability of the photo-Fenton oxidation process for RR-dye removal was done using a continuous mode under the influence of the variation of the

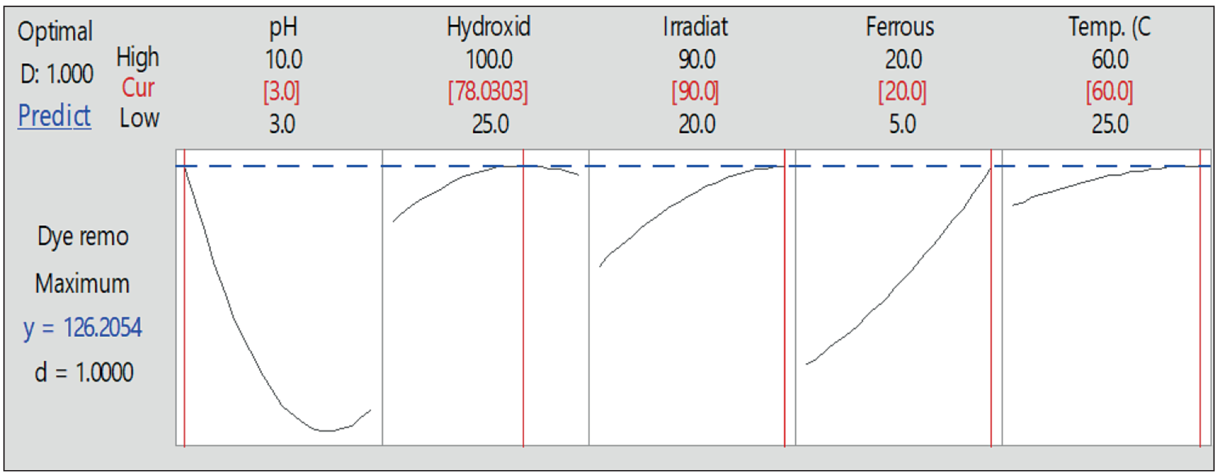

Figure 9. The optimization results of the batch-operating parameters of the RR-dye removal efficiency response for the treatment of synthetic wastewater

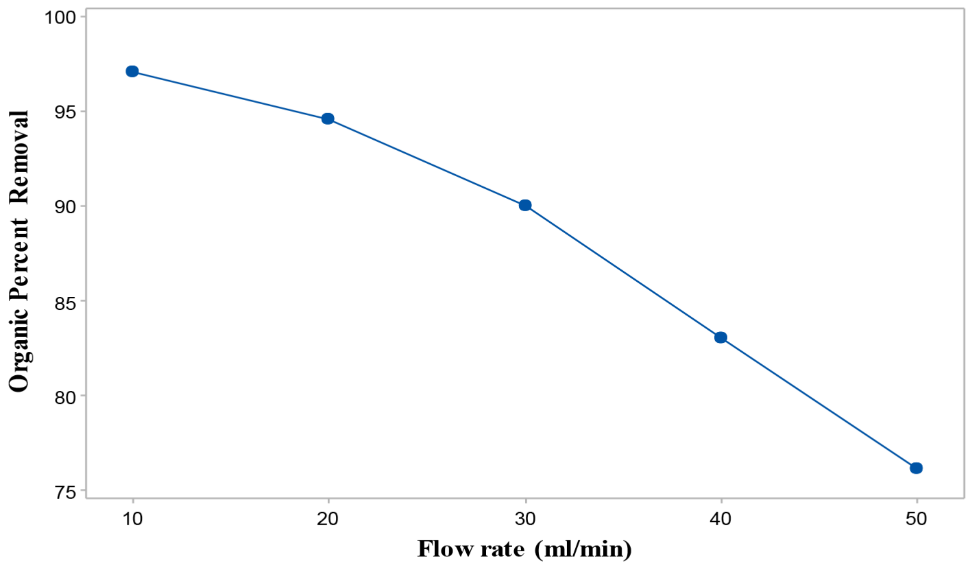

Figure 10. The influence of flow rate on the RR-dye removal; H_2O_2=78 ppm, Fe^{+2}=20 ppm, pH=7, 4 UV-lamp

flow rate. The flow rate values studied were 10, 20, 30, 40, and 50 mL/min, containing 40 ppm of dye's initial concentration using 4 UV lamps. Figure 10 revealed that removal efficiency minimized extensively when the flow rate increased.

At 10 mL/I of flow rate, the removal efficiency attained 97% then, it was minimized inversely with the increase of flow rate to reach 76% at 50 mL/l where the irradiation time between dye Reactive red and catalyst surface was abridged. These findings agreed with the results obtained by (Hassan and Al-zobai 2019).

CONCLUSIONS

This study presents essential findings of using photo-Fenton oxidation reactors. This work has investigated that batch and continuous system configurations might be an appropriate method to treat dye wastewater under the influence of several operating variables. In the batch system, all the organic compounds were removed compared to that of 82% obtained when the continuous system was used. The optimal values of the operational variables in the case of the batch system were 3, 78 ppm, 90 min, 20 ppm, and 60 °C for pH, hydrogen peroxide, irradiation time, ferrous sulphate, and temperature, respectively. The limits, light intensity, flow rate, and the number of UV lamps were the most significant intended for the squalor efficiency.

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