



Treatment of POME using Fenton oxidation process: removal efficiency, optimization, and acidity condition

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ABSTRACT

In this study, the performance of a Fenton oxidation process was evaluated for the treatment of high-concentrated palm oil mill effluent (POME). Experiments were designed using the central composite design model of the response surface methodology (RSM). Four independent variables (reaction time, H₂O₂ concentration, Fe²⁺ ions concentration, and initial solution pH) and two dependent responses (COD and final solution pH) were investigated. The results show that at a low Fe²⁺ concentration and pH of about 3, an acceptable COD removal efficiency was achieved. At optimum conditions of pH 3.5 and 90 min reaction time, COD removal exceeded 85% and was successfully optimized by RSM. A significant model ($p < 0.0001$) was obtained for final pH condition and statistically reached a satisfactory level with a correlation coefficient (R^2) of about 0.71. This study, therefore, demonstrates the capacity of Fenton process to successfully remove COD from high-concentrated POME under the right combination of process variables.

Keywords: Fenton process; POME; Oxidation; Response surface methodology; Final pH

1. Introduction

Palm oil plantation and processing produces various kinds of waste materials such as oil palm trunks, oil palm fronds, empty fruit bunches, palm-pressed fibers and palm oil mill effluent (POME) [1,2]. These waste materials constitute a significant disposal problem and require a special treatment process. POME is a highly concentrated wastewater from oil palm pro-

cessing and commonly found in oil palm producing nations. Malaysia, being among the key players (2nd) in global oil palm plantations and the leading exporter of vegetable oil, generates high amount of palm oil mill waste [3,4]. Therefore, there is a dire need to effectively manage the abundant waste materials from this industry for environmental and economic benefits.

Advanced oxidation process (AOP) has been widely used in the treatment of wastewater from

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various industries such as in food production, medical processes, oil palm industries, and leachate treatment [5–10]. Over the last decade, Fenton processes (Photo Fenton and Electro Fenton) have demonstrated effective reduction capacity of industrial wastewater organic and inorganic compounds at laboratory level [11]. Fenton processes have the capability to transform pollutants into non-toxic biodegradable substances [12]. The mechanism of the Fenton chemical process can be found in several studies [13–18]. Numerous studies have been conducted to optimize the Fenton, electro-Fenton, and photo-Fenton processes in wastewater treatment. However, studies on the optimization of POME are few. Experimental variables such as COD, color, and reaction time are reported for POME optimization by Fenton oxidation process but TSS, NH_3 , Fenton reagents dosage, reagent feeding mode, effect of reaction time, electrochemical oxidation reaction, and electrolysis are not yet reported and need tangible focus. Generally, chemical treatment of POME is costly and could neutralize the effect of the added chemicals [19]. However, Fenton oxidation requires only a small amount of ferrous sulfate and hydrogen peroxide to achieve an excellent result. The benefits of Fenton oxidation processes include low operation cost, relatively low treatment time, and high removal of organic pollutants [16,20–23].

Response surface methodology (RSM) is a statistical software which uses experimental data to determine optimum variable conditions of various processes [24]. It can develop experimental runs, predict best fit model, optimize process variables, and generate a standard deviation based on results calculated at various points in the design space [25]. Several studies have employed RSM for the analysis of leachate treatment based on selected variables [26–30]. Similarly, RSM have been applied to POME treatment [31–34]. Mohajeri et al. [29] used RSM to optimize the bioremediation of coastal sediments artificially polluted with weathered crude oil. Hamze et al. [35] applied RSM for biodiesel production from cooking oil waste. Isa et al. [36] utilized RSM for boron removal from produced water through electrocoagulation, whereas Ghafoori et al. [18] employed RSM to investigate the efficiency of sonophotolysis process in an external loop airlift sonophoto reactor in batch mode.

The acidic condition of raw wastewater is an important factor for effective treatment and plays a significant role in identifying the suitable ratio of chemical compounds used to treat the polluted medium. POME causes a variety of health and environmental risks without adequate treatment. Therefore, the aim of this study was to investigate the COD

removal efficiency and its optimization with observation on the final pH condition of post-treated POME oxidized by Fenton process. The effects of the independent variables (COD and final pH) are discussed.

2. Experimental

2.1. Sampling

POME was collected after biological pre-treatment in five open ponds in Nasaruddin SDN. BHD, located in Bota District in Bandar Seri Iskandar, Perak, Malaysia. The sample was collected manually according to Standard Methods [37]. It was transported to the laboratory and stored at 4°C in the cold room prior to use. The characteristics of the POME used in this study are presented in Table 1. Ferrous sulfate ($\text{Fe}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, 98%) and hydrogen peroxide (H_2O_2 30%); both from R&M marketing, Essex, UK were used as received.

2.2. Chemical analysis

The experiments were conducted in a 250-mL beakers. Solution pH was varied in the range 2–5 and adjusted using H_2SO_4 or NaOH . Reaction time was also varied in the range 30–150 min. An orbital shaker (Model 722, PROTECH-UK) with shaking speed in the range of 0–250 rpm was used. A 250-mL beaker containing a 100-mL solution of POME was placed on the orbital shaker and agitated at 150 rpm according to the experimental plan. After each experimental run, the final pH and COD concentration was measured according to the standard methods for the examination of water and wastewater (APHA, 2005). The experiments were triplicated for each run.

Table 1
Characteristics of post-treated POME^a

Parameters	Units	Value
Temperature	°C	25–30
pH	–	8.4
COD	mg/L	4,500
BOD	mg/L	580
TSS	mg/L	129.9
TN	mg/L	127
TOC	mg/L	213
Color	Pt-Co	2,260
DOE discharge limit	mg/L	80–200

^aPOME sample collected in July 2014, DOE: Department of Environment, Malaysia.

2.3. Design of experiments and data analysis

The four independent variables investigated in this study are H₂O₂ concentrations (g/L), Fe²⁺ ions concentrations (g/L), pH, and reaction time (min) as presented in Table 2. Each of the independent variables was studied at three levels (−1, 0, +1). A total of 30 experiments were conducted at various Fe²⁺/H₂O₂ concentrations according to the experimental plan. A control flask was also agitated on the orbital shaker. The dependent variables (COD and final pH) were considered as the response. Samples were agitated on the orbital shaker (150 rpm) and reaction time of 30–150 min. Afterward, the beakers were allowed to settle for 2 h prior to response measurement. The Central composite design (CCD) experimental design for the four independent variables investigated in this study is shown in Table 3.

The RSM software (Design Expert 8.0.7.1) was used for design, mathematical modeling, and optimization. Alpha value at ($p < 0.05$) was used to examine the analysis of variance (ANOVA), the goodness of fit, and the significance of each term in the fitted equations. The levels were selected based on preliminary study results and literature review.

3. Results and discussion

3.1. Degradation behavior of POME content

Table 3 shows the degradation of POME at various conditions. Fig. 1(a) represents the raw (control) POME sample, whereas Fig. 1(b) and (c) represents Fenton oxidation of POME at various Fe²⁺/H₂O₂ concentrations. In the control samples (Fig. 1(a)), organic substrate removal of about 12.6% was observed. This could be due to the default photo oxidation of nano-materials during the treatment process. Similar observation is reported elsewhere [29,32]. Experimental results (run no. 8 and 23) show that increasing Fe²⁺ concentration at low amount of H₂O₂ can enhance the degradation of POME. COD removal of 83.9 and 85% (Fig. 1(c)) was obtained at pH 2 (150 min) and 3.5

(90 min). On the other hand, run no. 10 had the lowest degradable content (62.7%) at 150 min, followed by run no. 1 which have 64.3% at 90 min reaction time (Fig. 1(b)). Although, both runs no. 10 and 1 have an initial pH of 5 and 3.5, the final pH was 2.86 and 2.21, respectively. Similar observation is reported elsewhere [9,29,37–41]. Fig. 2 illustrates Fenton reaction process and degradation at various experimental runs.

In Fenton process, pH value in the range of 2.7–3.5 is usually optimal for effective treatment. Below pH 2, formation of complex iron species and oxonium ions occurs and reduces process efficiency [42,43]. In this study, experiments conducted at pH 2 have a final pH of about 2.7. The production of hydroxyl radicals decreased for experiments conducted at pH ≥ 5 due to the formation of ferric-hydroxo complex [44–47]. However, a decrease in pH from 5 to 2.85 was noticed in our study and a good result was achieved under this condition. Thus, the optimum pH for Fenton oxidation of POME could be approximated to 3. A similar observation was made by Nasr et al. [16] who reported that the pH value decreased from 4.9 to 2.1 in their study. However, significant chemical reaction was observed at pH 3.

In complex organic wastewater, the degradation rate is directly proportional to substrate concentration [19]. AOPs, particularly Fenton processes, have been widely used for the enhancement of biological treated wastewater containing different organic and non-biodegradable compounds which are toxic to microorganisms [48–51].

3.2. RSM statistical proprieties testing

3.2.1. Regression model

CCD of RSM was employed to discern the output nature of the response surface software in the designed experiment and to explain the optimization level of the four independent variables as mentioned earlier. Table 3 (last column) shows the output results obtained from the experimental design software using

Table 2
Coded and actual values of variables used in the RSM

Factor	Symbol	Coded and actual variables level		
		Low (−1)	Center (0)	High (1)
H ₂ O ₂ conc. (g/L)	A	1.33	3.99	5.67
Fe ²⁺ ions conc. (g/L)	B	1.12	2.8	4.48
pH	C	2	3.5	5
Reaction time (min)	D	30	90	150

Table 3
The CCD experimental design in actual levels and its results

Run no.	Input: factors				Output: results			
	Reaction time (min)	pH	Fe ²⁺ conc. (M/L)	H ₂ O ₂ conc. (M/L)	COD removal (%)		Final pH value	
					Observed	Predicted	Observed	Predicted
1	90	3.5	0.05	0.03	64.3	57.45	2.2	2.21
2	90	3.5	0.05	0.04	70.5	76.76	2.5	2.49
3	30	2	0.08	0.05	77.0	77.16	2.5	2.49
4	150	2	0.08	0.05	65.9	65.86	2.2	2.21
5	90	3.5	0.05	0.03	77.8	79.77	2.6	2.59
6	30	5	0.02	0.05	75.1	75.0	2.7	2.62
7	90	3.5	0.07	0.03	76.7	81.58	2.0	1.99
8	150	2	0.02	0.05	83.9	82.81	3.1	2.98
9	60	3.5	0.05	0.03	77.2	74.88	2.6	2.59
10	150	5	0.02	0.01	62.7	65.69	2.8	2.86
11	120	3.5	0.05	0.03	77.2	77.38	2.6	2.61
12	30	2	0.02	0.01	75.6	77.38	2.6	2.61
13	30	5	0.02	0.01	74.4	77.35	2.5	2.49
14	90	3.5	0.05	0.03	80.4	75.12	2.6	2.61
15	30	2	0.08	0.01	79.5	77.38	2.6	2.61
16	150	5	0.08	0.01	76.3	64.06	2.0	1.99
17	150	5	0.08	0.05	73.5	65.29	2.9	2.98
18	30	5	0.08	0.01	73.0	75.53	2.2	2.2
19	150	5	0.02	0.05	78.8	79.65	2.6	2.61
20	90	3.5	0.05	0.03	78.6	80.07	2.6	2.75
21	150	2	0.02	0.01	80.2	77.75	2.5	2.49
22	30	2	0.02	0.05	72.6	76.38	2.5	2.53
23	90	3.5	0.05	0.02	85.0	83.21	2.9	2.86
24	90	3.5	0.05	0.03	77.2	74.69	2.5	2.46
25	30	5	0.08	0.05	77.9	77.38	2.6	2.61
26	90	3.5	0.05	0.03	65.0	62.91	2.1	2.12
27	90	4.25	0.05	0.03	71.4	76.12	2.2	2.2
28	90	2.75	0.05	0.03	26.5	45.39	2.1	2.12
29	150	2	0.08	0.01	78.3	77.38	2.6	2.61
30	90	3.5	0.04	0.03	75.3	77.38	2.7	2.61

empirical second-order quadratic polynomial model as expressed in Eq. (1):

$$Y = \beta_0 + \sum_{i=1}^k \beta x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i=1}^k \sum_{i \neq j=1}^k \beta_{ij} x_i x_{ij} + \varepsilon \quad (1)$$

where β_0 is the value of the fixed response (constant) at the central point of the CCD design; (β_i , β_{ii} , and β_{ij}) are the linear, quadratic, and interaction coefficient regression terms, respectively; x_i is the level of the independent variable; “ n ” signifies the number of independent variables and “ ε ” is error.

The ANOVA determines the significance of each coefficient. The probability ($p < 0.05$) and Fisher test

(F -test) indicates that all factors and their interactions in the experimental design are statistically significant at 95% confidence interval. The goodness of fit of the model was expressed by the correlation coefficient (R^2), adjusted R^2 , and predicted R^2 . The final regression model in terms of their coded factors is expressed in Eqs. (2) and (3) below:

$$\text{COD}(Y1) = 77.37 + 5.38A + 4.77B + 1.50C - 4.53D - 4.57AB + 4.23CD - 7.0C^2 \quad (2)$$

$$\text{Final pH}(Y2) = 2.60 + 0.29A - 0.033B - 0.07C - 0.014AC + 0.031BC - 0.18A^2 \quad (3)$$

where A for pH, B for H₂O₂, C for Fe²⁺ con., D for reaction time.

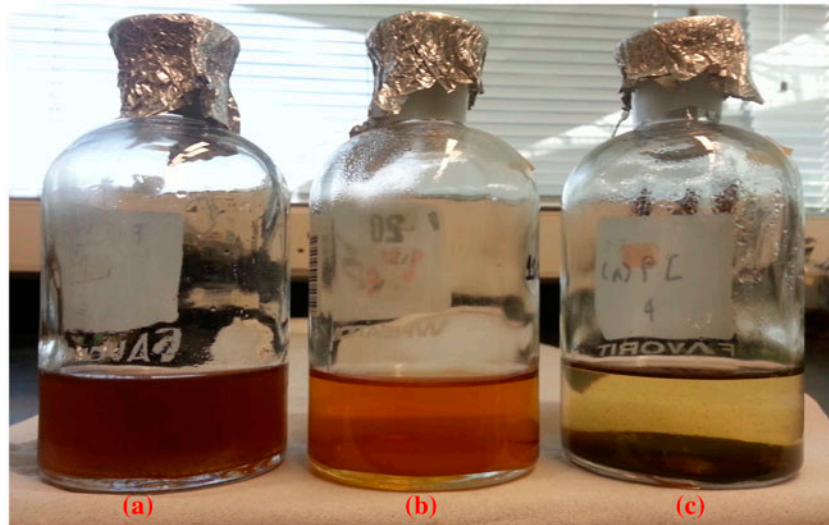


Fig. 1. POME samples: (a) the raw sample, (b and c) treated samples.

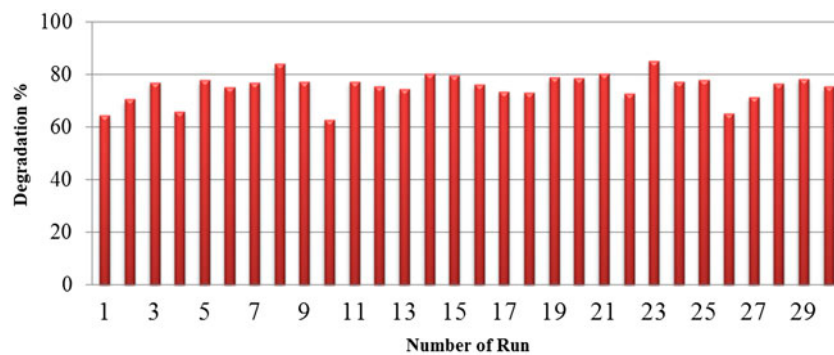


Fig. 2. Fenton reaction and degradation process of 30 run.

An excellent interaction among the tested variables was observed. For instance, pH and H_2O_2 (AB), Fe concentration and reaction time (CD), and Fe concentration and Fe concentration (C^2) showed good interaction.

Considerable interaction among the variables, such as pH and Fe^{2+} ions (AC), H_2O_2 concentration and Fe^{2+} ions (BC), pH and pH (AA), was also observed. The measured and predicted (Eqs. (2) and (3)) data are compared in Table 3. The proposed empirical model is suitable for predicting COD and final pH and demonstrated a reasonably good agreement with the quadratic model. The regression model in Eqs. (2) and (3) was used to derive the equation for testing the COD and final acidic (pH) condition of treated POME samples.

The COD regression equation, correlation coefficient (R^2), adjusted R^2 , and predicted R^2 were automatically generated and evaluated in Table 4 to test the fit of the model. The model F -value of 755 and its

alpha value (Prob. > F 0.0001) implies that the model is significant. Furthermore, a high correlation coefficient of 0.71 for COD and 0.97 for final pH suggests that more than 96.82% of the variances are attributable to the variables. Adjusted R^2 of 0.9599 and predicted R^2 of 0.9456 indicates that the model is linear and significant. Thus, only 3.18% of the total variance cannot be explained using this model.

The adequacy of the model was further evaluated by the Fisher test (F -test). The F -test obtained in this study is significant ($p < 0.05$). In this case A , B , C , D , AB , AC , BC , CD , A^2 , and C^2 are significant model terms. From a statistical point of view, the insignificant effects of factors and its interactions when p -values are higher than 0.05, must be ignored. Consequently, the model showed that the sample acidity (pH) had a significant effect on both COD and final pH of the study.

Table 4
RSM model fit summary output table for COD and Final pH

Statistical figure	Abbreviation	COD	Final pH
Mean	Mean	73.52	2.50
Standard deviation	Std. dev.	6.44	0.05
Coefficient of Determination	R^2	0.71	0.9727
Adjusted— R^2	Adj. R^2	0.61	0.9656
Predicted— R^2	Pre. R^2	0.1494	0.951
Coefficient of variance	C.V.	8.76	2.00
Adequate precision	AP	11.365	41.178
Predicted residual error sum of square	Press	2,642.93	0.10

Table 5
RSM/ANOVA output table for COD and Final pH

Source	Sum of squares	df	Mean square	F-value	Prob. > F/p-value	Remarks
<i>COD</i>						
Model	2,193.87	7	313.41	7.55	0.0001	Significant
A	477.91	1	477.91	11.51	0.0026	Significant
B	374.90	1	374.90	9.03	0.0065	Significant
C	37.28	1	37.28	0.90	0.3536	Insignificant
D	338.19	1	338.19	8.15	0.0092	Significant
AB	333.98	1	333.98	8.04	0.0096	Significant
CD	286.46	1	286.46	6.90	0.0154	Significant
C ²	345.17	1	345.17	8.31	0.0086	
Residual	913.32	22	41.51	–	–	
Lack of fit	899.39	17	52.91	18.99	0.0021	Significant
Pure error	13.93	5	2.79	–		
Cor Total	3,107.19	29				
<i>Final pH</i>						
Model	2.04	6	0.34	136.76	<0.0001	Significant
A	1.37	1	1.37	549.3	<0.0001	Significant
B	0.018	1	0.018	7.36	0.0124	Significant
C	0.08	1	0.08	32.2	<0.0001	Significant
AC	0.33	1	0.33	132.81	<0.0001	Significant
BC	0.16	1	0.16	6.28	0.0198	Significant
A ²	0.23	1	0.23	92.63	<0.0001	Significant
Residual	0.057	1	2.489e			
Lack of fit	0.057	23	3.181e			
Pure error	0.00	18				
Cor Total	2.1	295				

3.2.2. Analysis of variances

The COD and final pH ANOVA for the proposed quadratic model is presented in Table 5. The lack of fit model was significant (F -value 18.99) and (Prob. > F 0.0021). The lack of fit measures the error within the replicated experiments relative to pure error in the design space. The lack of fit is designed to determine whether the selected model is adequate to describe the observed data. The F -value of 18.99 implies the lack of fit is significant relative to the pure error. The

predicted R^2 value of 0.71 for COD and 0.9727 for final pH were in reasonable agreement with the adjusted R^2 value of 0.61 and 0.9656, respectively.

3.2.3. Adequate precision and variation coefficient value (CV)

The adequate precision (AP) for a good model should be >4. In this study, the AP value of 11.365 and 41.178 in Table 4 indicates that this model can

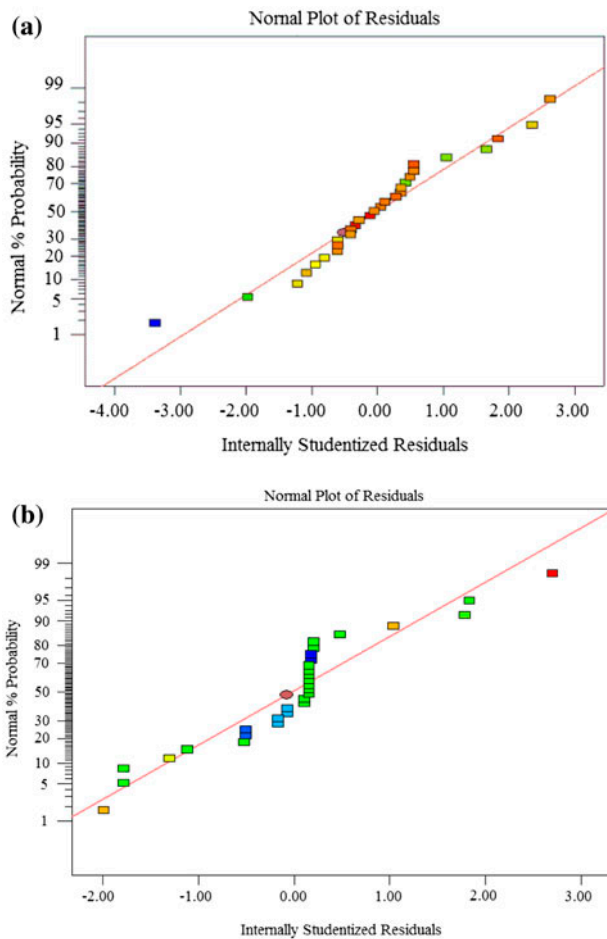


Fig. 3. Linear normal probability plot of residuals: (a) for COD and (b) for Final pH.

adequately fit into the design space. The coefficient of variation (CV) measures the reproducibility of the model. As a principle, the model can be reasonably reproduced if its CV is not greater than 10%. Hence, the low CV value of 8.76 and 2.0% obtained here indicates a high precision and reliability of the experiments.

3.2.4. Diagnostics Plot interpretation

Fig. 3(a) shows the linear COD plot of the predicted versus actual run in CCD. The plot has a goodness of fit and high R^2 (0.71 and 09,727). In fact, actual values represent the actual run of experiments in the lab, while the predicted values calculates an approximate function used for the current model. Residuals and normal percentage probability plot are illustrated in Fig. 3(b). Normal probability plot of the residuals may show non-normality in the error term (such as an S-shaped curve), which may be corrected by a transformation technique. Residual shows the difference between the observed value of a response (pH) and the value that is fitted under the theorized model. The small residual value of 0.10 in Table 4 for final pH, indicates that the model prediction is accurate regardless of the S-shaped curve of the data point's distribution. The high residual value of 2,642.93 for COD requires an adjustment.

3.3. Interaction of factors

The 3D graphical plot in Fig. 4 shows the interaction between Fe^{2+} and H_2O_2 for COD. The maximum

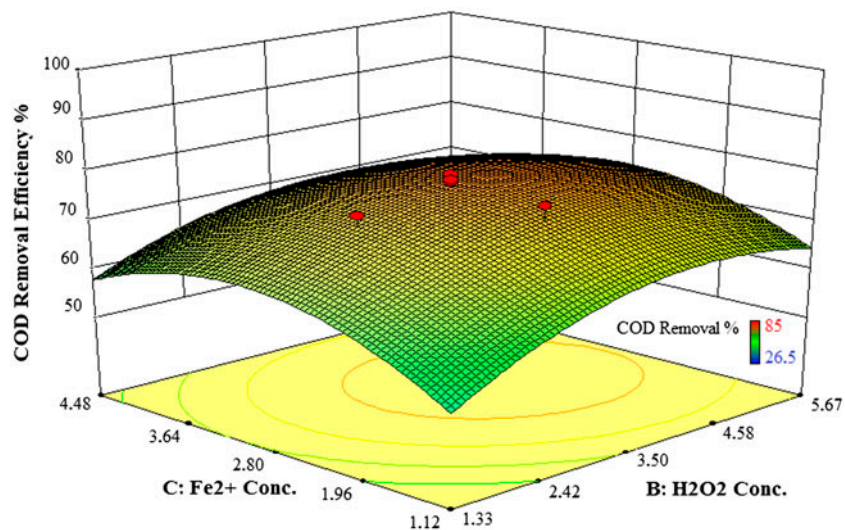


Fig. 4. COD removal efficiency.

Table 6
Diagnosed of the CCD model

Response name	Units	Analysis	Removal		Mean	Std. dev.	Ratio	Model
			Min.	Max.				
Y1	COD	%	26.5	85.0	73.61	10.38	3.21	Quadratic
Y2	Final pH	–	2.0	3.1	2.50	0.27	1.55	Quadratic

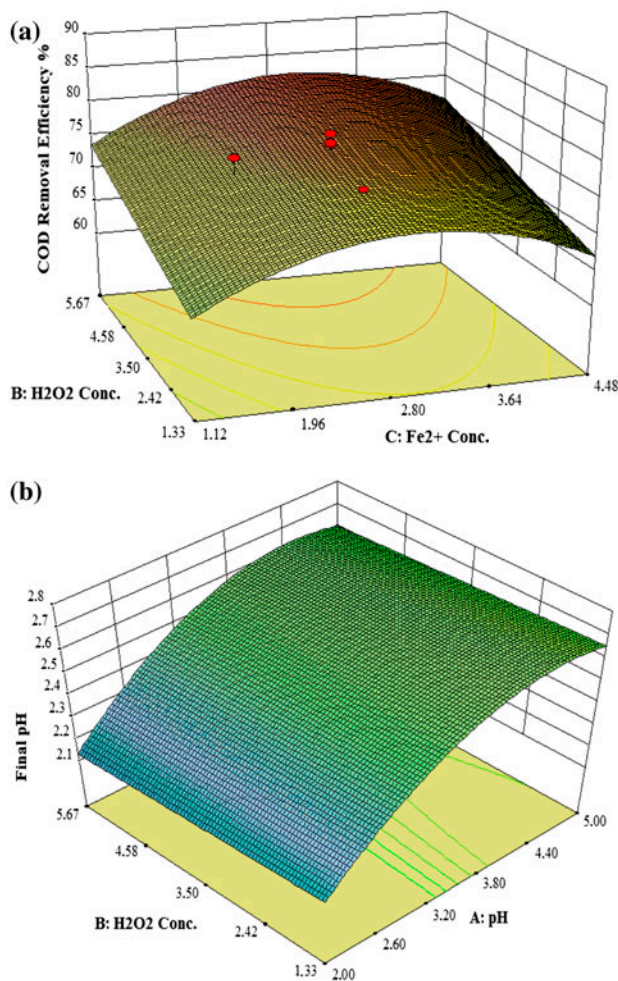


Fig. 5. Optimization result: (a) for COD and (b) for Final pH.

COD removal of 85% was achieved at a reaction time of 90 min and initial pH of 3.5 as shown in Fig. 4. The final pH for all factors was in the range of 2.6–2.85. Similar observation is reported elsewhere [52,53]. The RSM diagnosis of CCD model is shown in Table 6. The model predicts a final pH of about 2.0–3.1.

3.4. Final pH optimized condition and verification

The numerical optimization analysis based on desirability function of 1.00 was carried out for the overall experiments. A total of 90 (30 × 3) experiments was conducted to determine the optimum final pH and COD removal at optimum conditions. The desirability results presented in Fig. 5 clearly indicated that optimization was effective for initial Fe^{2+} concentration of 1.12 and 2.8 g/L at an H_2O_2 concentration of 3.5 g/L. The final pH of 2.85 and 2.65 for both Fe^{2+} concentrations of 1.12 and 2.8 g/L were significant as shown in Fig. 5(a) and (b) with no major difference observed. However, at low Fe^{2+} concentration of 1.12 g/L, the pH was almost 3.0 which implies that a low Fe^{2+} concentration is preferred in Fenton reaction. These two final pH values were close to pH 3.0. After the completion of the Fenton oxidation reaction, optimal removal efficiency occurred [16,54]. A COD maximum removal of about 85% was achieved in this study.

The experimental error was investigated for validation of experiments. The errors between predicted and actual values were calculated according to Eq. (4).

$$\text{Error} = \frac{\text{Actual value} - \text{predicted value}}{\text{Actual value}} \times 100 \quad (4)$$

An error percentage within $\geq 5\%$ indicates that the optimization process of RSM software was capable and reliable [55]. In this study, error values below 5% was achieved.

4. Conclusions

The results of the current work showed that low concentration of ferrous ions resulted in better COD removal efficiency. In addition, the initial pH was totally different when compared to the final pH at the end of the experiment. Maximum COD removal of about 85% was achieved in this study. Using the quadratic model, the optimum acidic condition was

closed to pH 3. The optimum pH for effective COD removal was found to be in the range of 3.0–3.5. This study has therefore demonstrated that the Fenton oxidation process has the capability to degrade organic and inorganic compounds commonly found in POME.

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