Fenton oxidation treatment of biodiesel wastewater: optimization using response surface methodology and MATLAB software

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Abstract

Fenton oxidation was utilized to treat biodiesel wastewater. The Box-Behnken experimental design and response surface methodology were applied to evaluate the effects of variables. MATLAB Software was executed to compute the optimum conditions for COD removal at all selected initial pH from the quadratic model. The three independent variables, namely initial pH, $FeSO_4$ concentration and H_2O_2 concentration affected the performance of the Fenton oxidation process. Chemical Oxygen Demand (COD) were selected as response variable. The significance of independent variables and their interaction were tested by the analysis of variance (ANOVA). The result revealed that H_2O_2 concentration was the main factor affecting the COD removal while initial pH and $FeSO_4$ concentration were considered as less significant factors. The optimal condition were found to be at initial pH 5.0909, 16.5253 g/l $FeSO_4$ and 231.8667 g/l H_2O_2 which could be predicted to obtain the removal efficiency of 103.7026% theoretically.

Keywords: Fenton, Biodiesel wastewater, Box-Behnken, Response surface methodology

Introduction

Nowadays large concern is increasing over the use of fossil resources, their cost, their maintained availability and their impact on global warming and pollution. Biodiesel or fatty acid methyl esters (FAME) is one of the most promising alternative fuels with many advantages since it is renewable, biodegradable, low emissions, high flash point and excellent lubricity. Biodiesel, in addition to decreasing the levels of pollutants, can be blended with diesel or used in pure form (Khan *et al.*, 2014). Biodiesel is produced from vegetable oils or fats through transesterification reaction with alcohols, like methanol and ethanol, in the presence of a homogeneous base catalyst, for instance, NaOH and KOH, to yield fatty acid alkyl ester and glycerol. The biodiesel production process with tranesterification reaction uses a large amount of water; 20-120 l per 100 l of biodiesel produced (Jaruwat *et al.*, 2010). Currently, Thailand has capacity of biodiesel production up to 2.4 ML/day causing the formation of at least 480,000 l/day biodiesel wastewater. Wastewater from biodiesel process consists of high level of oil and grease, high solid content and low content of nitrogen and phosphorus (Chavalparit *et al.*, 2009). Accordingly, the biodiesel industry has been forced to implement effective treatment technologies in order to achieve the quality standards related to environmental protection. Several methods based on physical, chemical and biological transformation have been developed to treat biodiesel wastewater. Advanced oxidation processes (AOPs) have been interesting for the treatment of wastewater from biodiesel industry, especially when the elimination of the hard-to-biodegrade organics remaining in the wastewater is required. AOPs generate high reactivity of hydroxyl radical ($^{\cdot}OH$) for the degradation of toxic organic pollutants. As one of the AOPs, Fenton oxidation process has been effectively used to treat various organic contaminants including highly toxic compound

(Pignatello *et al.*, 2006). In Fenton reaction, when Fe^{2+} co-exists, H_2O_2 is transformed to a hydroxyl radical ($^{\cdot}OH$), which is one of the most effective oxidants, according to Eq. (1).

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO^{-} + {}^{\cdot}OH \qquad (1)$$

Fe (II) acts as catalyst. The main pathway for Fe (II) regeneration is shown in Eq. (2)

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HO_2^{\cdot} + H^{+} \qquad (2)$$

However, appropriate pH for Fenton process is acidic. It is necessary to adjust the pH before treatment, hence, complicating the operation process and increasing the cost (Wang *et al.*, 2012). The main objective of this study was to investigate the application of Fenton oxidation in the treatment of biodiesel wastewater and determine the optimization of Fenton oxidation for the removal using response surface methodology and MATLAB Software.

Methodology

Material

Hydrogen peroxide solution (50 wt%), iron (II) sulfate heptahydrate, sulfuric acid and sodium hydroxide were all of analytical grade. All of these chemicals were used as received without further purification. Distilled water was used in all experiments.

Biodiesel wastewater characteristics

The Biodiesel wastewater used in this study derived from a biodiesel plant in Thailand. The biodiesel wastewater had COD of about 63,000 mg/L, pH 3.02 and pale white color.

Fenton experiments

Fenton experiment was conducted in 1 L beaker with 50 mL of biodiesel wastewater under magnetic stirring at room temperature. The initial pH of the biodiesel wastewater was adjusted to the desired value using 1M NaOH or 1M H_2SO_4 solution. Subsequently, a predetermined amount of catalytic ferrous sulfate ($FeSO_4{\cdot}7H_2O$) was added and the Fenton reaction was started by adding the desire amount of H_2O_2 (50%w/w). After certain reaction time, 5M NaOH solution was added dropwise to increase pH to about 7.5-8.5 to stop the reaction and precipitate the ferric hydroxide. After that, the sample was centrifuge for 15 min at 5000 rpm. Final sample of supernatant were analyzed for COD removal.

Analytical methods

COD measurements were performed by the closed reflux colorimetric method using an UV/Vis spectrophotometer (DR6000 HACH, USA)

Experimental design

A three-level-three-factor Box-Behnken design with 2 replicates was conducted. The variable parameters and their selected levels for the study of the COD removal efficiency (%) can be described in Table. 1.

Table 1: Experimental design of coded levels and independent variables

Factor	Variables	Level		
		-1	0	1
X_1	pH	2	5	8
X_2	H_2O_2 (g/l wastewater)	22.2	144.3	266.4
X_3	$FeSO_4$ (g/l wastewater)	4	14	24

Statistical analysis

The COD removal efficiency (%) was selected as the dependent response variable. A quadratic polynomial model explaining the relationship between independent variables and dependent response variables is in equation (3).

$$Y = \beta_0 + \beta_1X_1 + \beta_2X_2 + \beta_3X_3 + \beta_{11}X_1^2 + \beta_{22}X_2^2 + \beta_{33}X_3^2 + \beta_{12}X_1X_2 + \beta_{13}X_1X_3 + \beta_{23}X_2X_3 \quad (3)$$

Where, Y is the predicted response; β_0 is the constant coefficient of the model; β_1, β_2 and β_3 are the linear regression coefficients; β_{11}, β_{22} and β_{33} are the quadratic regression coefficients; β_{12}, β_{13} and β_{23} are the interaction regression coefficients.

Results and discussion

Regression analysis was employed on the data obtained from the designed experiments. Minitab Software V.16.2.2 was used to generate the second-order polynomial regression equation according to COD removal efficiency as shown in eq. (4).

COD removal efficiency

$$Y (\%) = 11.0001 + 4.0554X_1 + 0.5987X_2 + 1.5547X_3 - 0.4296X_1^2 - 0.0012X_2^2 - 0.0369X_3^2 - 0.0009X_1X_2 + 0.0314X_1X_3 - 0.0021X_2X_3 \quad (4)$$

Where X_1 is initial pH, X_2 is concentration of $FeSO_4$ (g/L wastewater), X_3 is the concentration of H_2O_2 (g/L wastewater) and X_1X_2, X_1X_3 and X_2X_3 are interactions of these parameters.

Table 2 shows analysis of variance (ANOVA) of the regression model (Eq.(4)) confirming that the quadratic model was highly significant, as was obvious from the calculated F value ($F_{cal} = 222.52$) was found to be greater than the tabulated F value ($F_{0.05, 9, 20} = F_{tab} = 2.39$) at the 5% significance level, indicating that the null hypothesis would be rejected. The coefficient of determination (R^2) of the models was 99.01%, which showed that the total variation data were well fitted between the experimental and predicted values of the response.

Table 2: ANOVA result of the quadratic models

Source	Df	Sum of squares	F-value	*p*-value	R^2
Model	9	13999.8	222.52	0	99.01%
Linear	3	11488.5	181.26	0	
Square	3	2448.7	116.76	0	
Interaction	3	62.5	2.98	0.056	
Error	20	139.8			

The 2-D contour plot of the COD removal efficiency of the Fenton oxidation (Fig. 1) showed the interaction effect of different independent variables on the COD removal efficiency (%). It is obviously seen from Fig. 1a and Fig. 1b that the initial H_2O_2 concentration had a positive effect on COD removal, whereas $FeSO_4$ concentration and initial pH affected very little on that value. The result revealed that the H_2O_2 concentration was the main effect on the COD removal efficiency due to the increase in $^{\cdot}OH$ concentration as a result of the addition of H_2O_2 (Sun *et al.*, 2008). Fig. 1c showed the effect of $FeSO_4$ concentration and initial pH on the COD removal. If $FeSO_4$ concentration was less than 6 g/L wastewater, increasing the initial pH had no effect on the COD removal. In contrast, if the $FeSO_4$ concentration increased more than 6 g/L wastewater, the initial pH had a positive effect. The result revealed that the COD removal efficiency increased with increased initial pH from 2 to 5, however, the COD removal decreased afterward. This is due to the fact that the oxidation potential of $^{\cdot}OH$ and also the solubility of iron species decrease with increasing pH. As the pH increases, Fe^{3+} starts to precipitate out in the form of amorphous $Fe(OH)_3$(s) retarding the generation of $^{\cdot}OH$ (Huang *et al.*, 2009).

(a) (b)

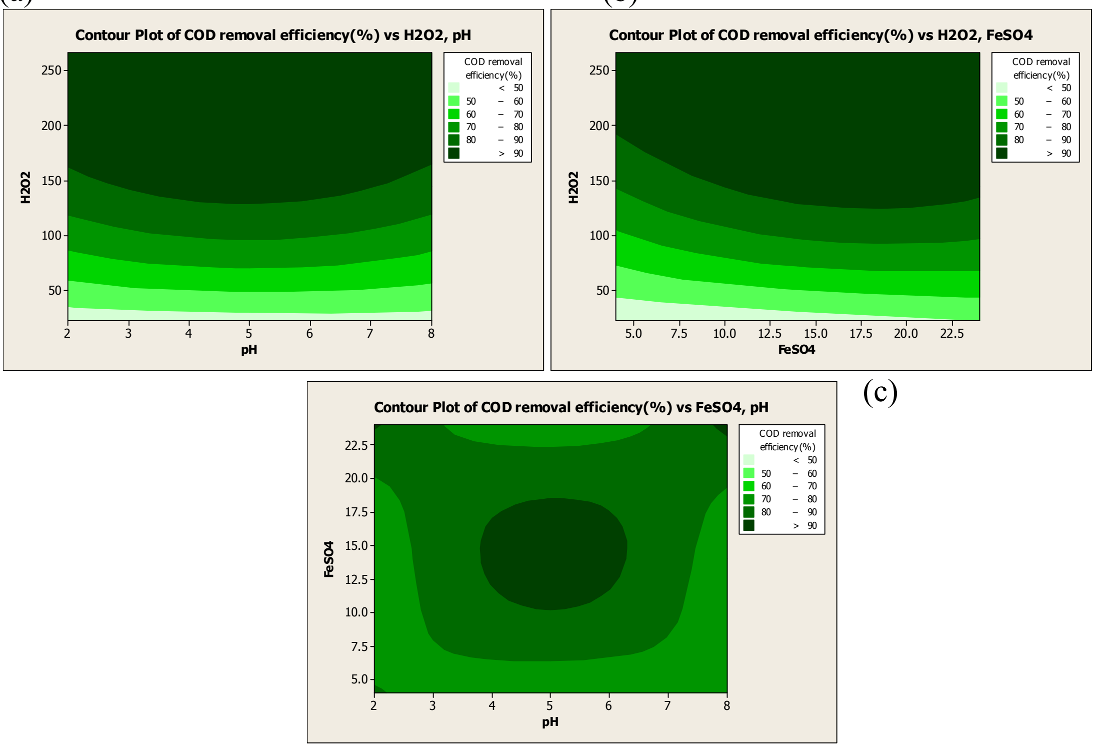

Figure 1: COD removal efficiency (%) correlating to (a) Interaction effect of H_2O_2 and initial pH, (b) Interaction effect of H_2O_2 concentration and $FeSO_4$ concentration and (c) Interaction effect of $FeSO_4$ concentration and initial pH

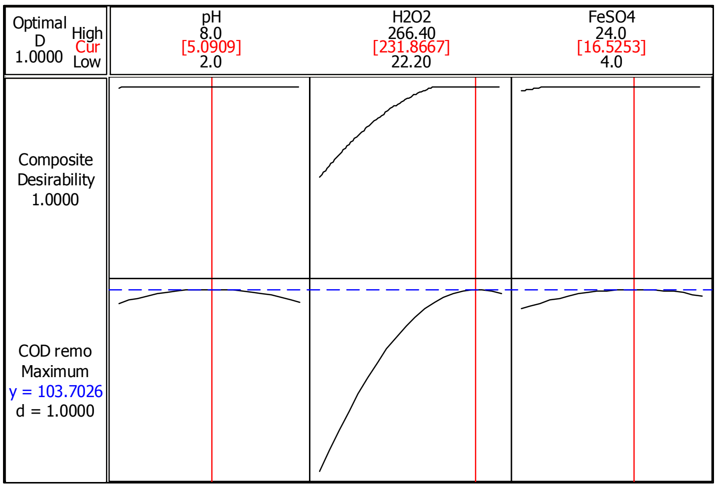

Figure 2: Response optimization of the COD removal efficiency (%)

The response optimization result for COD removal was shown in Fig 2. Under this optimal condition (pH 5.0909, H_2O_2 concentration at 231.86 g/L wastewater and $FeSO_4$ concentration at 16.5253 g/L wastewater), the removal efficiency of COD were predicted to be 103.7026%. Basically, the optimal pH was around 2-4 in the conventional Fenton process, depending on the kind of pollutant to be removed. However, the results of this experiment indicated that pH 5 was optimal since the addition of large dosage of $FeSO_4 \cdot 7H_2O$ dropped down the initial pH of the solution immediately to about 4. This behavior demonstrated that pH influenced the precipitation of iron. At pH 4, the majority of ferrous species was $Fe(OH)_2$, which was much more reactive than Fe^{2+} to catalyze H_2O_2 to free radical ($^{\cdot}OH$) (Pignatello *et al.*, 2006) . The quadratic model was further studied by measuring its accuracy. Optimal value and selected value of reaction conditions in the limited range were shown in Table 3. The experimental results were well fitted with those from predicted model of the COD removal efficiency.

Table 3: Validation of the COD removal efficiency

Initial pH	H_2O_2 concentration (g/L wastewater)	$FeSO_4$ concentration (g/L wastewater)	The COD removal efficiency (%)		
			Experimental result (avg.value from 2 duplicate)	Predicted result	error (%)
5.0909	231.8667	16.5253	97.8571	103.7206	5.65
3.02 (no adjust pH)	234.6116	15.6755	96.9047	102.1694	5.15

MATLAB (The Mathworks, inc ver. 7.10) computing environment was chosen to compute the optimum conditions for the COD removal efficiency in term of initial pH from the predicted model. Fig. 3 showed the optimum conditions of H_2O_2 concentration and $FeSO_4$ concentration for the maximum COD removal at all selected initial pHs. It revealed that optimal initial pH was around 5 for the maximum COD removal. At initial pH more than 5 or less than 5, the COD removal was decreased. The decrement in COD removal at pH less than 3 could be explained by inhibition of $^{\cdot}OH$ formation was due to the decrease of the soluble amount of Fe^{3+} that was in equilibrium with other iron species; $Fe(OH)^{2+}$ and $Fe(OH)_2^{+}$ (Rodrigues *et al*., 2009). Both of $Fe(OH)^{2+}$ and $Fe(OH)_2^{+}$ forming at low pH could react slowly with H_2O_2 and produced less amount of $^{\cdot}OH$ (Gallard et al., 1998). On the other hand, at pH more than 5, the COD removal decreased because of the formation of amorphous $Fe(OH)_3(s)$. In Fig. 3b, when initial pH increased, the system required less H_2O_2 concentration for the maximum COD removal. In contrast, when initial pH increased, the system required more $FeSO_4$ concentration for the maximum COD removal because Fe^{3+} started to precipitate out in the form of amorphous $Fe(OH)_3(s)$. The formation of $Fe(OH)_3$ decreased the dissolved Fe^{3+} concentration as shown in Fig. 3c.

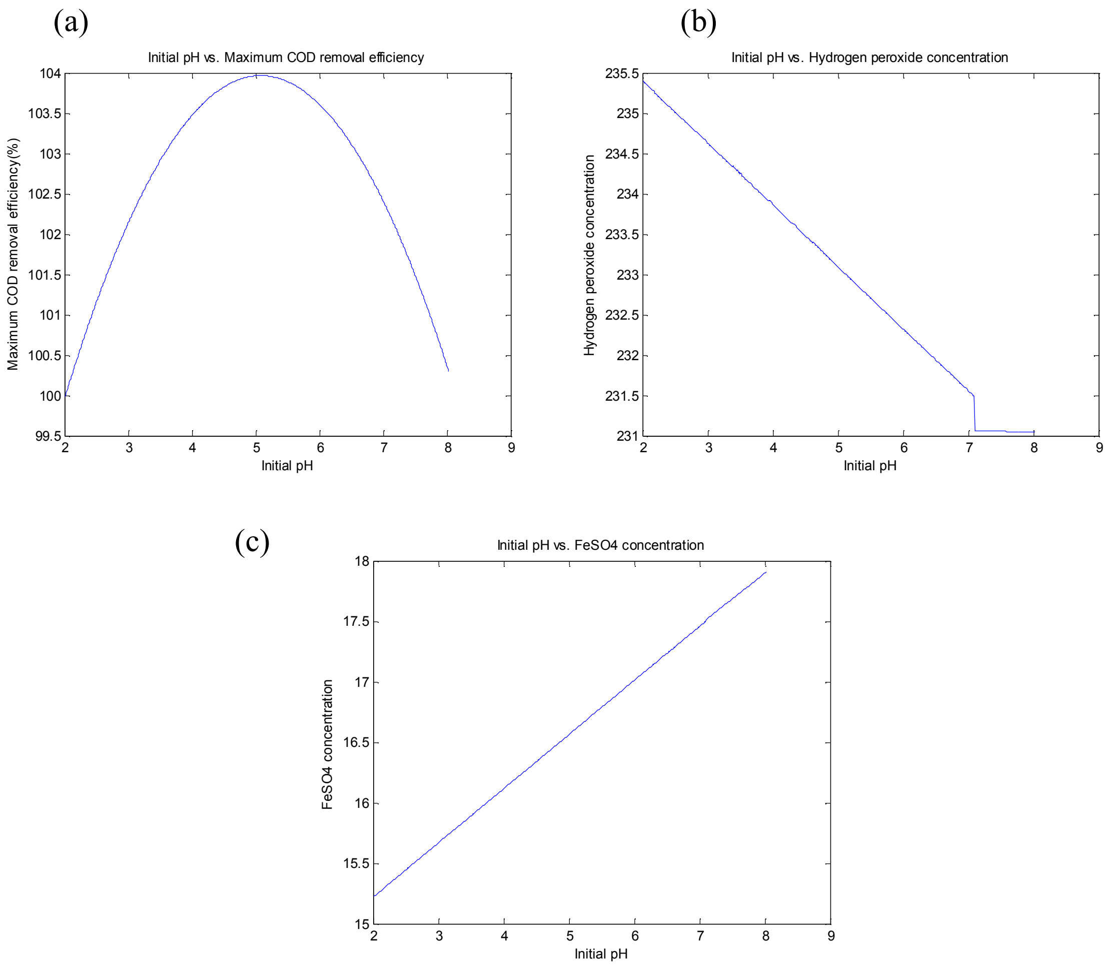

Figure 3: Interaction plotting of (a) initial pH versus maximum COD removal efficiency, (b) Intial pH versus H_2O_2 concentration and (c) Initial pH versus $FeSO_4$ concentration

Conclusion

The COD removal through Fenton oxidation has been investigated. Box-Behnken design and response surface methodology (RSM) were powerful tools to determine the significant parameters and predict the optimum conditions to maximize the process performance with high significance and high R^2 coefficients. Under the studied condition, H_2O_2 concentration was found to be the factor affecting on COD removal while the other factor had less significant effect. Optimum $FeSO_4$ concentration, H_2O_2 concentration and initial pH for the process were 16.5253 g/L wastewater, 231.86 g/L wastewater and 5.0909, respectively, Under this condition, COD could be removed up to 97.8571%. In practical use, if we use initial pH of 3.02 (no need to adjust), hydrogen peroxide about 234.61 g/L (Fig. 3b) and ferrous sulfate about 15.67 g/L (Fig. 3c), COD could be removed up to 96.9047%, which was nearly the COD removal of the optimum conditions. It revealed that we can reduce amount of sodium hydroxide used to adjust the initial pH and also reduce the step of pH adjustment before biodiesel wastewater treatment. Furthermore, numerical method employing MATLAB software was proved to be a right solution to evaluate the optimum condition for maximum COD removal at all the initial pHs.

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