Optimization of Photo-Fenton Oxidation of Sulfidic Spent Caustic by using Response Surface Methodology

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Abstract—This paper investigated the degradation of sulfidic spent caustic by using photo-Fenton oxidation process. Response surface methodology was employed to study the interaction effect between process parameters namely ferrous ion and H2O2 dosage towards the oxidation efficiency of sulfidic spent caustic. Hence, the best conditions for photo-Fenton process were determine based on the developed empirical model. By comprehensive studies, the optimal conditions of photo-Fenton reaction are at dosage ratio Fe/H2O2 and H2O2/COD of 0.07 and 1.84 correspondingly.

Keywords: sulfidic spent caustic, photo-Fenton oxidation, sulfide oxidation, response surface methodology

I. INTRODUCTION

Biogas and gases such as hydrogen sulfide and carbon dioxide are the most commonly found in hydrocarbon streams. The presence of gases normally sulfur-based compound in petroleum products will likely increase the corrosiveness of the crude feedstock and render harmful and severe reaction upon combustion [1, 2]. Consequently, caustic solution has been utilized as a scrubbing medium to remove the acid gas components from the feedstock. The acidic mixture will be converted into ionic state mainly sodium sulfide, sodium carbonate, sodium bicarbonate and sodium hydroxide [1]. An improvement in terms of odour and colour has been identified upon the use of caustic scrubbing in refinery operation. Unfortunately, the spent caustic produced from this process become quite harmful due to its complex toxicity mixture. This waste inhibits rather high COD and BOD indicating that it will adversely affect the environment if it is hastily released into the water bodies. Apart from that, due to its complex composition, spent caustic has been classified as hazardous waste under the US Resource Conservation and Recovery Act [3]. Therefore, a great concern must be taken on the disposal ways of spent caustic from refinery operations to provide an environmentally acceptable effluent to be discharged.

Some of the existing applications for the disposal of spent caustic are biological treatment and wet air oxidation. Biological treatment is said to be the most widely employed in treating sulfidic spent caustic. Sulfide-oxidizing bacteria; Thiobacillus denitrificans is notoriously utilized in reduction of sulfur compound in the wastewater. Despite being an economical treatment option available, high BOD and COD content of sulfidic spent caustic seems to hinder the effectiveness of biological treatment of spent caustic [4 – 8].

Currently, the employment of advanced oxidation processes (AOPs) in dealing with highly toxic recalcitrant contaminants is being acknowledged. AOPs are well known for their ability to oxidize almost all reduced material present in the water bodies without restriction to a specific classes or group of compounds. It involves generation of strong oxidants mainly hydroxyl radicals (OH•) that reduce the toxic organic compounds into simpler and biodegradable end products [9 – 11]. Hydroxyl radicals are capable to react with dissolved constituents in wastewater thus promoting series of oxidation reaction until the constituents are completely mineralised [10]. A number of AOPs are available in remediation of toxic constituents including reaction with ozone, H2O2, ultraviolet irradiation, Fenton’s reagent as well as photo-Fenton oxidation. Among these, the capability of photo-Fenton oxidation in the degradation of toxic contaminants has been investigated thoroughly.

Photo-Fenton oxidation is an improvement to Fenton’s reagent with the addition of irradiation source. Several studies reported that the degradation efficiency of the oxidation process is improved under UV illumination when compared to the ordinary Fenton reaction [12 – 14]. Consequently, the presence of UV illumination in photo-Fenton oxidation process allows photo reduction of ferric species into ferrous ion according to the following reactions [9, 12, 14]:

\[ \text{Fe}(III)OH^{2+} \xrightarrow{hv} \text{Fe}(II) + OH \cdot \] (1)

\[ \text{Fe}(III)(RCO}_2\text{)}^{2+} + \text{hv} \xrightarrow{\text{LMTO}} \text{Fe}(II) + \text{CO}_2 + R \cdot \] (2)

As shown in the above equation, photo reduction of ferric species will not only benefit in the reduction in iron catalyst usage by recycling of ferrous ion, but also provides extra hydroxyl radical into the system [9, 12, 15, 16]. Apart from that, effect of illumination in photo-Fenton will concomitantly promote photolysis of H2O2 which resulted in the generation of additional hydroxyl radicals in the system as shown in equation (3) [12]:

\[ \text{H}_2\text{O}_2 \xrightarrow{hv} 2\text{OH} \cdot \] (3)

Thus, based on these unique attributes possessed by this process, it caught a huge interest as a treatment option for various types of wastewater. Several studies have been
reported on the application of photo-Fenton oxidation process, including the treatment of petroleum refinery sourwater [17], methomyl degradation [18], treatment of dye and textile effluent [12, 15, 19], treatment of distillery wastewater [20] and degradation of phenol [21].

Response surface methodology (RSM) is a statistical tool that being applied in the modelling and analysis of a response in which influenced by several variables [15, 16, 20, 22]. It integrates the interacting effect between number of process variables in order to give the optimal response [15]. RSM is widely being applied in the designing, modelling, analyzing new study and also improvement to the current process. Furthermore, employment of RSM in numerous studies and also in industrial stage proven that it is a reliable tool.

As far as we are concerned, no work has ever been done on the photo-Fenton oxidation of sulfidic spent caustic wastewater. Hence, this study aims at investigating the reliability of photo-Fenton process in treating sulfidic spent caustic wastewater. In addition, RSM was applied to evaluate the effects of each variable towards the performance of oxidation process. The effect of the dosage of H$_2$O$_2$ and ferrous ion were thoroughly investigated on the removal of COD as well as sulfide in the treated wastewater. Concomitantly, the optimal condition for spent caustic treatment was established from the optimization process.

II. EXPERIMENTAL DESIGN AND METHODS

A. Sample preparation
A synthetic sulfidic spent caustic wastewater was prepared to simulate the effluent originating from a refinery operation. In order to attain uniformity throughout the experiment, the synthetic sulfidic spent caustic was prepared by utilization 10mM sulphide as well as 75mM phenol in distilled water [8]. The role of phenol in the synthetic spent caustic is as non-sulfur pollutant in the wastewater. The characteristics of the synthetic wastewater are summarized in Table 1. As evident from the table, the wastewater possesses a high level of pH, COD and sulfide concentration.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>11.42 - 12.37</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>3183 - 5658</td>
</tr>
<tr>
<td>Sulfide (mg/L)</td>
<td>469 - 614</td>
</tr>
</tbody>
</table>

B. Reagents and materials
Hydrogen peroxide was supplied by Merck, at the concentration of 30-35% (v/v), and was stored under refrigeration. 95-98 wt% sulphuric acid grade AR and crystallized phenol with reagent grade ACS were obtained from Scharlau. Extra pure iron (II) sulphate heptahydrate was from Daed Jung Chemicals, Korea and sodium sulphide-flake was from Systerm. All chemicals and reagents were all analytical grade and were used without further purification. Distilled water was used in all experiments.

C. Analytical methods
The total aqueous sulphide concentration in the spent caustic sample was determined using methylene blue method. The changes in the chemical oxygen demand (COD) in the spent caustic was measured by means of dichromate reflux method. Both analysis were conducted using DR5000 Spectrophotometer.

D. Experimental procedure
Photo-Fenton oxidation of sulfidic spent caustic wastewater was conducted in a magnetically stirred reactor with a working volume of 250 mL. The photo-reactor consists of a two-unit UV-germicidal lamp G48T6/L/U covered with quartz sleeve with dimension of 1143 x 1219 x 660 mm with 50 W each. The lamp was located in the centre of the reactor in a vertical manner. The whole assembly was covered with aluminium sheet.

Initially, pH adjustment was performed by using 95-98 wt% H$_2$SO$_4$ or 1N NaOH solutions to obtain an acidic environment of pH 3.5±0.1. The pH used is based on the findings of previous studies [23, 24]. In acidic environment, the interaction between H$_2$O$_2$ and Fe$^{2+}$ enhanced thus resulting in the production of more hydroxyl radical. The required amount of reagents was determined according to the initial COD concentration of the wastewater. Fe$^{2+}$ catalyst was first added into the reaction mixture followed by H$_2$O$_2$ after a 5 min lapse. Thereafter, the reaction solution was promptly located under the UV lamp which was turned on 15 min before the start of reaction to obtain a stable and constant light emission. The photo-Fenton oxidation reaction was initiated with the addition of H$_2$O$_2$ into the system. The photo-Fenton reaction was performed at ambient temperature and pressure.

Samples were taken regularly at a predetermined interval up to 40 min reaction time. Samples pH were re-adjusted to 7 followed by sedimentation of ferric precipitate for 30 min. The results of the COD and sulfide removal were statistically analyzed using Design Expert 6.0.6.

E. Experimental design and statistical analysis
Central composited design (CCD) which is one form of RSM was employed as a statistical tool for the experimental design as well as process optimization. The design consisted of 2$^k$ factorial points augmented with 2$^k$ axial points and a centre point where k is the number of variables involved [25]. Accordingly, 13 experiments were conducted with 4 factorial points, 4 axial points and 1 centre point. For more accurate result, the centre point was repeated five times. This type of wastewater is unstable and the value of initial COD fluctuates from time to time. Thus, in the present work, ratio of H$_2$O$_2$/COD and Fe/H$_2$O$_2$ were considered as the independent variables while COD and sulfide concentration were the dependant variables. The values of the independent variables were obtained from extensive literature survey as well as the preliminary studies conducted with the synthetic spent caustic. The range and level of the variables in the RSM studies are presented in Table 2.
TABLE 2. Experimental ranges and levels of the independent variables

<table>
<thead>
<tr>
<th>Factor</th>
<th>-α</th>
<th>-1</th>
<th>0</th>
<th>+1</th>
<th>+α</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/H₂O₂</td>
<td>0</td>
<td>0.01</td>
<td>0.105</td>
<td>0.2</td>
<td>0.239</td>
</tr>
<tr>
<td>H₂O₂/COD</td>
<td>0.379</td>
<td>1</td>
<td>2.5</td>
<td>4</td>
<td>4.621</td>
</tr>
</tbody>
</table>

The data from the experimental work was analyzed by using a second-order-polynomial model [15, 20, 26].

\[ Y = b_0 + \sum b_i X_i + \sum b_{ii} X_i^2 + \sum b_{ij} X_i X_j \]  

(4)

The model was used to obtain the interaction between the dependent and independent variables. In this equation, \( Y \) signifies the predicted dependent variables (response) while \( X_i \), \( X_j \) represent the independent variables that being considered in the process while \( b_0 \), \( b_i \), \( b_{ii} \), \( b_{ij} \) represent the interaction coefficients. The constructed models were being thoroughly analyzed by means of analysis of variance as well as regression analysis. The results were presented in terms of both three dimensional plot and contour plot.

III. RESULT AND DISCUSSION

A. Response surface analysis

Table 3 shows the experimental design and results based on CCD for photo-Fenton oxidation of sulfidic spent caustic. The responses were evaluated in terms of percentage removal of COD and sulfide concentration in the treated wastewater.

As can be seen from the table, both factors show a significant effect in the percentage removal of COD. The COD removal increased when higher ratio of Fe/H₂O₂ and H₂O₂/COD was applied. For instance, at constant ratio of 0.11, the COD removal increased from 60.31 – 94.90% with the increasing H₂O₂/COD ratio of 0.38 to 4. The similar result was obtained when the ratio of Fe/H₂O₂ varied from 0.01 to 2 where the COD removal accelerated from 57.86 – 94.44% at constant H₂O₂/COD ratio of 1. On the other hand, over 99% sulfide removal was detected in the experimental work despite the ratio of factors being employed.

![Table 3](image)

The results were further analyzed using Analysis of Variance (ANOVA) with the aids of Design Expert. The analysis started with full quadratic terms. The ANOVA of the reduced model is given in Table 4.

In analyzing the model, the value of Prob > F less than 0.05 imply that the model is significant. On the other hand, values greater than 0.1 indicate that the model terms are insignificant. Hence, in this study the Prob > F values of 0.0064 and 0.0009 for COD and sulfide removal respectively, indicating that all the developed model terms were significant. The square of correlation coefficient for each of the responses was denoted by the coefficient of determination, \( R^2 \). The closer value of \( R^2 \) to 1, the better the model fits the data. The highest \( R^2 \) value was obtained from sulfide removal in which is 0.8822. Adequate precision shows the signal to noise ratio that measures the range of predicted response upon possible errors. A ratio greater than 4 is desirable. In this case, both developed models showed an adequate signal to noise ratio. Concurrently, low values of standard deviation 0.19 – 18.91% indicate a good precision and lower dispersion of the models.

![Table 4](image)
Hence, the COD removal in photo-Fenton process can be represented by a reduced quadratic model as shown in equation (5).

\[
\text{COD} = 36.9941 + 746.9853 \times (\text{Fe}/\text{H}_2\text{O}_2) - 2201.0494 \times (\text{Fe}/\text{H}_2\text{O}_2)^2
\]  

(5)

Based on the constructed model, the main, second order effect and interaction effect that consist of factor \( \text{H}_2\text{O}_2/\text{COD} \) was found to be statistically insignificant, thus excluded in the main model. Therefore, the removal of COD in photo-Fenton oxidation process can be concluded to be solely dependent on Fe/\( \text{H}_2\text{O}_2 \). The contour and three dimensional plots for the COD removal with respect to Fe/\( \text{H}_2\text{O}_2 \) and \( \text{H}_2\text{O}_2/\text{COD} \) within the design space are illustrated in Fig. 1.

As can be seen from this figure, the efficiency of COD removal is increasing with the increase in the Fe/\( \text{H}_2\text{O}_2 \) ratio. However, ratio of \( \text{H}_2\text{O}_2/\text{COD} \) denoted an insignificant effect towards the performance efficiency. Similar behaviour of \( \text{H}_2\text{O}_2 \) consumption in photo-Fenton process was obtained by previous studies on photo-Fenton degradation process on variety of wastewater [17, 20, 26, 27]. This condition maybe due to the sufficient amount of \( \text{H}_2\text{O}_2 \) was present in the system. The excess amount of \( \text{H}_2\text{O}_2 \) remain in the solution may become a hindrance in the COD reading of the final effluent. Thus, lower removal of COD was obtained.

The relationship of both factors towards the sulfide removal was shown in equation (6). Based on the model, it can be concluded that the second order effect of factor Fe/\( \text{H}_2\text{O}_2 \) gave a negligible effect on the removal efficiency.
Figure 2. Contour (a) and three dimensional (b) plots of the model for sulfide removal as a function of Fe/H$_2$O$_2$ and H$_2$O$_2$/COD of sulfidic spent caustic by using photo-Fenton oxidation.

Sulfide = 97.849 + 6.1545*(Fe/H$_2$O$_2$) 
+ 1.175*(H$_2$O$_2$/COD) 
- 0.1337*(H$_2$O$_2$/COD) 
-1.8576*(Fe/H$_2$O$_2$)* (H$_2$O$_2$/COD) 

(6)

From the developed model, contour and three dimensional plots of sulfide removal are constructed as shown in Fig. 2. The figure indicates that higher removal efficiency of sulfide compound could be achieved by increasing the dosage concentration of both Fe/H$_2$O$_2$ and H$_2$O$_2$/COD. As can be seen from the plots a minimum sulfide removal of 98.88% was detected at Fe/H$_2$O$_2$ and H$_2$O$_2$/COD ratio of 0.01 and Fe/H$_2$O$_2$ of 1. This result indicates that even if a smallest ratio of Fe/H$_2$O$_2$ and H$_2$O$_2$/COD are employed, it still resulted in high sulfide removal.

B. Optimization of photo-Fenton oxidation processes

In this present study, process optimization was carried out by using RSM. The main purpose of this stage is to determine the optimal condition for photo-Fenton oxidation of sulfidic spent caustic with respect to minimal usage of reagent as well as highest possible response. Study by Benatti (2006) stated that by maximizing the COD removal in photo-Fenton process, it will results in minimal sludge formation. Thus, by implying the optimum condition into a real case scenario, a possible reduction in chemical cost as
The optimization process was performed by verifying the desired goal for each of the factors and responses. Hence, a “minimum” goal was defined for each factor Fe/H₂O₂ and H₂O₂/COD while a “maximum” was declared as the goal for the removal of COD and sulfide. Consequently, the result for process optimization is summarized in Table 5.

Based on the table, it has been estimated that 80% and 100% removal of COD and sulfide accordingly can be achieved in photo-Fenton process under working condition of Fe/H₂O₂ = 0.07 and H₂O₂/COD = 1.84. The predicted responses from optimization process were validated through experimental run. A series of experiments for photo-Fenton process were conducted according to the specified working condition based on Table 5. Hence, the data obtained were compared to the ones predicted by the models. The result are presented in Table 5.

As is evident in Table 5, the actual values of sulfide removal obtained from the experiments did not have much divergence from the predicted value. Correspondingly, it confirmed the validity of the polynomial model developed for the removal of sulfide in sulfidic spent caustic by photo-Fenton process. On the other hand, much higher percentages of COD removal were achieved experimentally when compared to the predicted value form the model. The slight difference might be the influenced of the initial COD condition of the wastewater before photo-Fenton oxidation occurred. However, the empirical model for COD removal is still acceptable and can be further utilized.

IV. CONCLUSION

Application of photo-Fenton oxidation in treating sulfidic spent caustic wastewater resulted in remarkable removal efficiency of COD and sulfide compound. Two modified quadratic equation were developed for COD and sulfide removal to describe the effect of each factors towards the oxidation process. From the process optimization, the optimal conditions for photo-Fenton oxidation were found to be at dosage ratio of Fe/H₂O₂ = 0.07 and H₂O₂/COD = 1.84. Under these conditions the maximum removal of 100% and 97% for the sulfide and COD removal correspondingly. In photo-Fenton process, the optimal ratio of H₂O₂/COD plays an important role whereby excess amount of H₂O₂ in the system may lead to interference in the final COD value. This study can be used as a reference for further research and application of this process in the future.

TABLE 5. Comparison between the predicted and experimental value of COD and sulfide removal in photo-Fenton process

<table>
<thead>
<tr>
<th>Predicted value</th>
<th>Experimental data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/H₂O₂</td>
<td>H₂O₂/COD</td>
</tr>
<tr>
<td>Run 1</td>
<td>0.07</td>
</tr>
<tr>
<td>Run 2</td>
<td>0.07</td>
</tr>
<tr>
<td>Run 3</td>
<td>0.07</td>
</tr>
</tbody>
</table>

as sludge treatment cost would be possible.

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REFERENCES


