Performance of Fluidized bed Fenton process in Degrading Acid Blue 113

M M Bello¹,² and A A Raman¹,*
¹ Department of Chemical Engineering, Faculty of Engineering, University of Malaya, Kuala Lumpur, 50603, Malaysia
² Centre for Dryland Agriculture, Bayero University, P M. B. 3011, Kano, Nigeria.

E-mail: azizraman@um.edu.my and mmbello.cda@buk.edu.ng

Abstract. The performance of a fluidized bed Fenton process in degrading Acid Blue 113 (AB 113) was investigated. Fluidized bed Fenton process is a modification of conventional Fenton oxidation, aimed at reducing sludge generation and improving process performance. Response surface methodology was used to study the effects of operational parameter on the color removal from the dye. Dimensionless factors, Dye/Fe²⁺, H₂O₂/Fe²⁺ and pH were used as the independent variables in Box-Behnken Design (BDD). Reduced quadratic model was developed to predict the color removal. The process could remove up to 99% of the initial color. The most significant factor for color removal was found to be Dye/Fe²⁺, followed by H₂O₂/Fe²⁺. Unlike conventional Fenton, the initial pH of the solution does not have a significant effect on the color removal.

1. Introduction

The environmental pollution arising from the use of synthetic dyes in textile and other industries has become a source of concern globally. Textile industry produces large quantity of dyes-containing effluents which are highly polluting, posing a threat to the environment [1]. Organic dyes have complex structures and high stability, making them difficult to degrade through the conventional methods [2]. Consequently, the treatment of dyes-containing effluents has attracted researchers’ interest.

Various technologies such as adsorption [3], coagulation-flocculation [4], biological process [5], membrane technology [6] have been investigated for dye removal. These methods have some limitations in textile wastewater treatment. The physicochemical methods usually concentrate the pollutants into solid/liquid side streams [1] whereas biological process is relatively slow and usually convert the dye to some intermediates [7]. Thus, the search for effective treatment technologies for dye removal has been intensified.

Advanced oxidation processes (AOPs), which are based on the generation of reactive oxidants, are considered promising technologies for the degradation of recalcitrant dyes [8]. Among AOPs, Fenton oxidation has received wide attention due to its effectiveness, simplicity of the process and availability of Fenton’s reagent [9]. The conventional Fenton oxidation is based on a catalytic reaction between Fe²⁺ and H₂O₂. In a general form, the reaction can be written as shown in equation 1 [10].

\[ M^{n+} + H_2O_2 \rightarrow M^{n-1} + OH^- + HO (M = Fe) \]  

Despite the effectiveness of Fenton oxidation in degrading recalcitrant pollutants, it faces some limitations which have hindered its large-scale applications. Fenton oxidation is pH dependent and favors a narrow range of operational pH (3 – 4). This is because the production of HO, which are
responsible for oxidizing the pollutant, is enhanced at lower pH [11]. Another limitation is the production of ferric sludge which requires further treatment and disposal [12]. Many approaches, such as heterogeneous Fenton and Fenton-like processes, have been taken to address these limitations. Recently, the use of fluidized bed technology to reduce sludge generation in conventional Fenton has received interest [13–16]. In fluidized bed Fenton (FBF), solids are used which provide surface for the precipitation of iron oxide and hence, lower sludge generation.

In this work, the performance of FBF process in the degradation of an azo dye, AB113 was investigated. Response Surface Methodology (RSM) was used to design the experiment and investigate the effects of operational parameters. RSM is a multivariate statistical analysis tool that can be used to design experiment, develop empirical models and study the effects of operational parameter [17]. Among the design approaches in the RSM, Box-Behken Design (BBD) is considered suitable as it has a low number of required experimental runs [18]. Thus, BBD was employed in this work to design the experiments and develop the RSM model for color removal from the Acid Blue 113.

2. Methodology

2.1. Chemicals

The chemicals used were purchased from Sigma-Adrich and include H$_2$O$_2$ (33 %), FeSO$_4$.7H$_2$O, H$_2$SO$_4$, NaOH, SiO$_2$ (0.2 – 1 mm) AB113 (dye content = 50%). All the chemicals were of analytical grades and used without further purification. Distilled water was used in all samples preparation.

2.2. Experimental setup

The schematic diagram of the FBF process is shown in Figure 1. It consists of a reservoir, recirculation section, magnetic pump and a flow meter. The reactor is a glass column of 135ml capacity and 30 cm height. The magnetic pump was used to pump the dye solution from the storage tank to the reactor at a flow rate of 0.21 mL/min. Glass beads were packed at the bottom of the reactor to a height of 4 cm to act as distributors. SiO$_2$ was placed above the glass beads to a height of 6 cm. Internal recirculation was used to control the fluidization of the carriers. The desired amount of Fe$^{2+}$ was added into the system in form of FeSO$_4$.7H$_2$O. The Fenton process was initiated by the addition of H$_2$O$_2$. Samples were collected at pre-determined intervals and the pH of the sample was raised above 10 with NaOH to stop the reaction.
2.3. Analysis

The analysis was done according to the Standard Methods for the Examinations of Water and Wastewater [19]. Color removal from the dye solution was measured using a UV Spectrophotometer (Spectroquant® Pharo 300, Merck, Germany). The color was measured as absorbance at 464 nm wavelength. The percent color removal is reported as the difference between the initial absorbance ($A_o$) and absorbance at a time, $t$ ($A_t$) as shown in equation 2.

$$\text{% Color removal} = \frac{A_o - A_t}{A_o} \times 100$$  \hspace{1cm} (2)

2.4. Experimental Design

Design Expert software (Stat-Ease, Inc., USA; Version 8.0.7.1) was used for the RSM analysis. BBD was used to design the experiment, develop empirical models and investigate the effects of the operational parameters on the process performance. The operational parameters considered are $[\text{Dye/Fe}^{2+}]$, $[\text{H}_2\text{O}_2/\text{Fe}^{2+}]$ and pH. The range of these parameters and their coding are shown in table 1.

| Independent variables | Coded | Low Actual Value | High Actual Value |
|-----------------------|-------|------------------|-------------------|
| $[\text{Dye/Fe}^{2+}]$ (wt/wt) | A     | 10               | 50                |
| $[\text{Fe}^{2+}/\text{H}_2\text{O}_2]$ (wt/wt) | B     | 5                | 25                |
| pH                    | C     | 3                | 9                 |

Figure 1. Experimental setup
3. Results and Discussion

3.1. Model fitting and ANOVA

The BBD suggested a total of 17 runs with 5 center points and 12 non-center points. Table 2 shows the experimental and predicted response based on the BBD. The highest experimental color removal (99.51%) is slightly lower than the highest predicted color removal (100.53%). However, it can be observed that experimental and predicted responses are nearly the equal.

| Run | Dye/Fe$^{2+}$ (wt/wt) | Fe$^{3+}$/H$_2$O$_2$ (wt/wt) | pH | Color removal (%) | Exp | Pred |
|-----|-----------------------|-----------------------------|-----|-------------------|-----|------|
| 1   | 30.00                 | 15.00                       | 6.00 | 91.35             | 90.32 |
| 2   | 10.00                 | 15.00                       | 9.00 | 99.20             | 100.53|
| 3   | 50.00                 | 5.00                        | 6.00 | 71.28             | 71.77 |
| 4   | 10.00                 | 25.00                       | 6.00 | 99.51             | 99.38 |
| 5   | 10.00                 | 15.00                       | 3.00 | 98.77             | 99.41 |
| 6   | 50.00                 | 25.00                       | 6.00 | 85.34             | 86.68 |
| 7   | 30.00                 | 15.00                       | 6.00 | 90.07             | 90.32 |
| 8   | 30.00                 | 5.00                        | 9.00 | 83.50             | 83.60 |
| 9   | 30.00                 | 25.00                       | 3.00 | 94.21             | 94.15 |
| 10  | 50.00                 | 15.00                       | 3.00 | 84.28             | 83.46 |
| 11  | 50.00                 | 15.00                       | 9.00 | 78.01             | 77.87 |
| 12  | 30.00                 | 15.00                       | 6.00 | 90.12             | 90.32 |
| 13  | 30.00                 | 25.00                       | 9.00 | 93.05             | 91.91 |
| 14  | 10.00                 | 5.00                        | 6.00 | 98.65             | 97.67 |
| 15  | 30.00                 | 15.00                       | 6.00 | 90.62             | 90.32 |
| 16  | 30.00                 | 5.00                        | 3.00 | 85.45             | 85.84 |
| 17  | 30.00                 | 15.00                       | 6.00 | 90.43             | 90.32 |

3.1.1. ANOVA for color removal

The color removal was found to fit a reduced quadratic model (equation 3). The ANOVA for the model is shown in table 3. The fitness of the model is determined by the P-values of the model, lack of fit, adequate precision measure and R$^2$. For the model to fit, the model must be significant (p value < 0.0500) and the lack of fit needs to be insignificant (p value > 0.1000). It can be seen that the model is highly significant (P value < 0.0001) while the lack of fit is insignificant (P value = 0.0822). On the other hand, the adequate precision (48.917) is higher than the minimum desirable value (4) indicating that the model can be used to navigate the design space. The adjusted R$^2$ is also in reasonable agreement with the predicted R$^2$. Figure 2 shows the graph of predicted versus experimental COD removal. It can be seen that a straight line is obtained, further indicating the agreement between the predicted and the experimental response.

Furthermore, the ANOVA shows that [Dye/Fe$^{2+}$] and [H$_2$O$_2$/Fe$^{2+}$] have significant effects on the color removal. The effect of pH on the color removal is also significant. The interaction of [Dye/Fe$^{2+}$] and [H$_2$O$_2$/Fe$^{2+}$] has a highly significant effect on the color removal. The quadratic term of [H$_2$O$_2$/Fe$^{2+}$] also has a significant effect on the color removal.
Table 3. ANOVA for the Color removal.

| Source     | Sum of Squares | df  | Mean square | F value   | P value  | Remark   |
|------------|----------------|-----|-------------|-----------|----------|----------|
| Model      | 956.89         | 6   | 159.48      | 184.46    | <0.0001  | Highly Sig. |
| A-Dye/Fe   | 745.28         | 1   | 745.28      | 861.99    | <0.0001  | Highly Sig. |
| B-H2O2/Fe  | 138.00         | 1   | 138.00      | 156.26    | <0.0001  | Highly Sig. |
| C-pH       | 10.01          | 1   | 10.01       | 11.58     | 0.0067   | Sig       |
| AB         | 43.55          | 1   | 43.55       | 50.37     | <0.0001  | Highly Sig. |
| AC         | 11.22          | 1   | 11.22       | 12.98     | 0.0048   | Sig       |
| B²         | 8.83           | 1   | 8.83        | 10.22     | 0.0096   | Sig.      |
| Residual   | 8.65           | 10  | 0.86        |           |          |           |
| Lack of fit| 7.54           | 6   | 1.26        | 4.55      | 0.0822   | Not Sig.  |
| Pure error | 1.11           | 4   | 0.28        |           |          |           |
| Cor total  | 965.54         | 16  |             |           |          |           |
| Adeq precision | 48.917    |     |             |           |          |           |
| R²         | 0.9910         |     |             |           |          |           |
| Adjusted R²| 0.9857         |     |             |           |          |           |
| Predicted R²| 0.9527       |     |             |           |          |           |

**Color removal** (%): \( +99.95 - 0.56[Dye/Fe] + 0.35[H_2O_2/Fe] + 0.46pH + 0.02[Dye/Fe][H_2O_2/Fe] - 0.03[Dye/Fe]pH - 0.01[H_2O_2/Fe]pH \) \( (3) \)

In equation 3, positive model terms represent synergetic effect on the COD removal while negative terms indicate antagonistic effects on the color removal. Therefore, \([H_2O_2/Fe]\), pH and the interaction of \([Dye/Fe^{2+}]\) and \([H_2O_2/Fe^{2+}]\) contribute positively to the color removal. On the other hand, \([Dye/Fe^{2+}]\), interaction of \([Dye/Fe^{3+}]\) and pH and the interaction of \([H_2O_2/Fe^{3+}]\) and pH have antagonistic effects on the color removal.

**Figure 2.** Predicted versus actual color removal
3.2. Effects of operational parameters
One of the most challenging aspects of Fenton process is the selection and optimization of operational parameters. Thus, understanding the effects of operational parameters on the performance of FBF is necessary for process control. In this section, the effects of operational parameters on COD and color removals by the FBF process are discussed.

The effects of Dye/Fe$^{2+}$, H$_2$O$_2$/Fe and pH on the color removal were investigated. Figure 3 shows the 3D plots of the color removal as a function of (a) Dye/Fe and H$_2$O$_2$/Fe and (b) Dye/Fe$^{2+}$ and pH. It can be seen that the color removal decreases as Dye/Fe$^{2+}$ increases from 10 to 50 (Fig 3 a). This is because the amount of Fe decreases as the Dye/Fe$^{2+}$ increases since the dye concentration was kept constant. Thus, there is insufficient Fe$^{2+}$ to catalyze the production of OH. Also, the color removal increases as the H$_2$O$_2$/Fe$^{2+}$ increases from 5 to 15. However, when the H$_2$O$_2$/Fe$^{2+}$ was increased from 15 to 25, the color removal decreases, albeit slightly. This could be due to complexation caused by excess H$_2$O$_2$. These complexes can increase the color of the solution. On the other hand, the effect of solution pH is not very significant. From Figure 3 (b), it can be seen that the color removal did not change significantly when the pH was increased from 3 to 9. This could be due to the heterogeneous reaction induced by the iron crystallization.

Figure 4 shows the perturbation plot for the color removal. The perturbation plots compare the effects of all factors at a particular point in the design space. A steep slope or curvature in a factor shows that the response is sensitive to that factor. A relatively flat line shows insensitivity to change in that particular factor. In this case, the perturbation is plotted at the center point of the design space. From figure 4, it can be seen that the color removal is most sensitive to Dye/Fe$^{2+}$, followed by H$_2$O$_2$/Fe$^{2+}$. On the other hand, the perturbation of pH is nearly flat, indicating that the color removal is not sensitive to the solution pH.

(a)  (b)

Figure 3. 3D plots for the effects of (a) Dye/Fe$^{2+}$ vs H$_2$O$_2$ and (b) Dye/Fe$^{2+}$ and pH
4. Conclusion

This study investigated the performance of FBF process in the degradation of a model dye, AB113. RSM was found to be a suitable tool for designing the FBF process and studying the effects of operational parameters. The FBF process could remove up to 99% of the initial color of the dye. The color removal can be predicted by a reduced quadratic model developed through the BBD-RSM. The most significant parameter affecting the performance of the FBF process is Dye/Fe$^{2+}$. The effect of solution pH on the color removal was found to be insignificant. This study shows that FBF process can be a promising technology for the degradation of textile effluents.

References
[1] Rajasimman M, Babu S V and Rajamohan N 2017 J. Taiwan Inst. Chem. Eng. 0 1–11
[2] Carvalho S S F and Carvalho N M F 2017 J. Environ. Manage. 187 82–8
[3] Raghunath S, Anand K, Gengan R M, Kumar M and Maity A 2016 J. Photochem. Photobiol., B Biol. 165 189–201
[4] Lau Y Y, Wong Y S, Teng T T, Morad N, Rafatullah M and Ong S A 2014 Chem. Eng. J. 246 383–90
[5] Malachova K, Rybkova Z, Sezimova H, Cerven J and Novotny C 2013 Water Res. 47 7143–8
[6] Liu C, Mao H, Zheng J and Zhang S 2017 J. Memb. Sci. 530 1–10
[7] Bilinska L, Gmurek M and Ledakowicz S 2016 Chem. Eng. J. 306 550–9
[8] Cai M, Su J, Zhu Y, Wei X, Jin M, Zhang H, Dong C and Wei Z 2015 Ultrason. Sonochem. 28 302–10
[9] Chen S, Wu Y, Li G, Wu J, Meng G, Guo X and Liu Z 2016 Appl. Clay Sci. 136 103–11
[10] Kouraichi S, El-Hadi Samar M, Abbessi M and Boudouh H 2015 Catal. Sci. Technol. 5 1052–64
[11] Malik P K and Saha S K 2003 Sep. Purif. Technol. 31 241–50
[12] Anotai J, Chen C, Bellotindos L M and Lu M 2012 Bioresour. Technol. 113 272–5
[13] Bello M M, Abdul Raman A A and Purushothaman M 2017 J. Clean. Prod. 141 1492–514
[14] Aghdasinia H, Bagheri R, Vahid B and Khataee A 2016 Environ. Technol. (United Kingdom) 37
[15] Garcia-Segura S, Bellotindos L M, Huang Y-H, Brillas E and Lu M-C 2016 J. Taiwan Inst. Chem. Eng. 0 1–15
[16] Chen T-C, Matira E M, Lu M-C and Dalida M L P 2016 Int. J. Environ. Sci. Technol. 300 1–12
[17] Sukriti, Sharma J, Chadha A S, Pruthi V, Anand P, Bhatia J and Kaith B S 2017 J. Environ.
[18] Ain N, Talib A, Salam F, Azah N, Ainliah S, Ahmad A and Sulaiman Y 2017 *J. Electroanal. Chem.* 787 1–10

[19] APHA 1992 Standard Methods for the Examination of Water and Wastewater *Water Environ. Fed.* 18th 9–45

Manage. **190** 176–87