OPTIMIZATION OF SIMAFIX RED DYE DECOLORIZATION BY USING ADVANCED OXIDATION PROCESS: PHOTO-FENTON

Nga Thi Dinh[1, *], Vu Phuong Thu[1], Mark Daniel G. De Luna[2]

[1]*HCMC University of Natural Resources and Environment, 236B Le Van Sy, Ward 1, Tan Binh District, Hochiminh City, Vietnam*

[2]*Department of Chemical Engineering, College of Engineering, U.P. Diliman, 1101 Quezon City, The Philippines*

[*]Email: dtnga@hcmunre.edu.vn

Received: 15 August 2016; Accepted for publication: 10 November 2016

ABSTRACT

This study investigated the Photo-Fenton process in textile wastewater treatment by using textile synthesis wastewater made of Symafix Red Dye solution. The aim of the study was to investegate the factors that influent to the photo-Fenton process such as contact time, pH, H_2O_2 and Fe^{2+}conectrations, and UVexposure in order to research the optimum values of this process.Treatment of textile wastewater was carried out at ambient temperature in a batch reactor. As a result, the second-order is suitable for the reaction of removing color by using Photo –Fenton processes. The removal efficiencies decreased when we increased the concentration of Fe^{2+} from 7.162 mM to 14.162 mM. When we increased the H_2O_2 concentration from 0.037 mM to 0.11mM, the removal efficiencies slightly decreased. The optimum value of pH is pH = 3. At the optimum of pH value and minimum the concentration of Fe^{2+} and H_2O_2 the removal efficiency could reach up to 95.82 %.

Keywords: textile wastewater, optimization, photo-Fenton process, hydroxyl radicals.

1. INTRODUCTION

The development of textile industry has been giving to the human a lot of money and satisfy fashion requirement. Beside the benefit of this industry, its environmental impacts have been more and more concerned. The textile industry consumes a considerable amount of water and a huge of chemicals in the manufacturing process [1]. Textile manufacturing consumes over 700,000t of approximately 10,000 kinds of dyes and pigments annually worldwide. It has been reported that up to 20 % of the dye used are discharged as industrial effluents during the textile dyeing and finishing processes without previous treatment [2]. Generally, the textile wastewater exhibits intense color, high chemical oxygen demand (COD), fluctuating pH, suspended particles, and the presence of chlorinated organic compounds, surfactants [1, 3, 4]. The organic compounds which contained in textile wastewater are not easily biodegradable. The discharging uncompleted treatment of this kind of wastewater in to the environmental can make seriously affectin toxic and carcinogenic to aquatic ecosystems [3, 5]. Therefore, it is necessary to find an effective way to treat well this kind of wastewater and deal with its environmental concernment. Various chemical, physical, and combined processes, such as elimination by adsorption onto activated carbon, coagulation by a chemical agent, ozone oxidation, ion exchange, etc. have been applied for the treatment of dye waste effluents [6]. Among textile wastewater treatment technologies, advanced oxidation processes (AOPs) is the most commonly and effectively. The main mechanism of AOPs process is use the special chemical reagents, physical factors to product Hydroxyl radical (OH•), highly reactive species generated in sufficient quantities by AOPs, Hydroxyl radical (OH•) have the ability to oxidize the majority of the organics present in the wastewater effluents [7, 5]. Common AOPs involve Fenton, Fenton like processes, ozonation, and electrochemical oxidation, photolysis with H_2O_2 and O_3, and TiO_2 photocatalysis [8]. Fenton process involves application of iron salts and hydrogen peroxide to produce hydroxyl radicals. Production of HO• radicals by Fenton reagent occurs in in the reaction below:

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

The mount of HO• will be increased via photochemical reaction in the UV/Fenton processes. Fenton reagent with UV light, the regeneration of Fe^{2+} and production of new HO• radicals, follows by the reactions below:

$$H_2O_2 + UV \rightarrow HO\bullet + HO\bullet \quad (2)$$

$$Fe^{3+} + H_2O + UV \rightarrow HO\bullet + Fe^{2+} + H^{+} \quad (3)$$

The main objectives of this study are (1) to determine the three primary factors that influent to Fenton process are: pH; Iron concentration; and H_2O_2 concentration. From that we determine the optimum of pH, Iron concentration, and H_2O_2 concentration for the chosen dye in using photo Fenton process, and (2) compare the removal efficiency of Fenton and Photo Fenton processes at optimum values.

2. MATERIALS AND METHODS

2.1. Reagents and Equipment

The dye which used to make synthesis textile wastewater is Simafix Red dye (Red dye SF 3B). This dye was used without further purification. Ferrous Sulphate $(FeSO_4).7H_2O$ (Merk). Hydro Peroxide (H_2O_2) (30 % w/w) (Merk). The solutions H_2SO_4 0.01 M, NaOH 0.01 M were used to adjust pH value for experiments. In this study, we also used the solution of NaOH 0.1 M to stop the reaction and store samples. All solutions were prepared with deionitedwater.

The equipment used for experiments including: pH meter was used to determine and adjust pH value of the reactor. Chemicals were balanced by analytical balance. Mini UV-Vis 1240 equipment was used to determine the absorption value and base on Abs values we can calculate the concentrations of dye contained in the solution. UV- lamp 20 W was used as UV source.

2.2. Experiment procedure

In this study, dye concentration was maintained at 500 ppm. The vary factors are pH; Iron concentration and H_2O_2 volume. Iron concentrations are 7.162 mM; 10.144 mM; and 14.32 mM. The pH values are 3; 5; and 7. The volumes of H_2O_2 were 0.037 mM; 0.073 mM; and 0.110 mM. All experiments were done at ambient temperature in 600 mL beakers, which were filled 500 ml of 500 ppm Simafixred dye solution. After adjusting pH value, the ferrous ion was put into the solution and stirred the solution for dissolving Iron. The final step is addition of hydrogen peroxide to the beaker.

The reactor was continuously stirred at 500 rpm in the entire of experiment period. The duration of each experiment was 60 min.Ten samples were taken and test: The first one is the sample of dye solution, the second one is the sample at the starting experiment (without UV), 8 more samples were taken at the time 5; 10; 15; 20, 30; 40; 50; and 60 (minutes). Each 1ml-sample was taken out from the beaker determined absorption value by UV – Vis.

2.4. Design of Experiment

The optimization of operating conditions was done using Box-Behnken design (BBD), a three level design was used to fit second- order models. The design has the advantage of having very efficient number of runs to fit the model. Design- Expert 7.0 software (Stat-Ease, Inc., Minneapolis, USA) was used to determine the number of experiments needed to optimize and analyze the system. Three important parameters namely: pH, Fe^{2+} and H_2O_2, were studied and optimized using BBD. A total 15 experimental runs were conducted with three replicates at the center point.

3. RESULTS AND DISCUSSION

Table 1 shows a summary of the decolonization efficiency of photo-Fenton process operated for 1 hour. Results showed a minimum degradation of 82.1 % was obtained at an initial Fe^{2+} and H_2O_2 concentration 1.744 mM and 0.073 mM respectively with an initial pH of 7. The maximum removal on the other hand was achieved at an initial concentration of 10.744 mM for Fe^{2+} and 0.037 mM for H_2O_2 at pH 3. At these conditons 97.66 % removals was observed for the photo-Fenton process.

Table 1. Dye Removal Efficiency for Photo-Fenton Process with the dye concentration was 500 ppm.

Run	Initial [Fe^{2+}] mM	Initial [H_2O_2] mM	Initial pH	% Removal
1	14.32	0.073	7.00	83.3
2	14.32	0.037	5.00	90.00
3	14.32	0.110	5.00	89.79
4	10.744	0.037	3.00	97.66
5	10.744	0.037	7.00	82.10
6	10.744	0.073	5.00	95.76
7	10.744	0.110	7.00	87.74
8	10.744	0.110	3.00	94.65
9	7.162	0.110	3.00	93.88
10	14.32	0.073	3.00	91.52
11	7.162	0.073	7.00	92.19
12	7.162	0.037	5.00	90.16
13	7.162	0.110	5.00	91.60
14	10.744	0.073	5.00	90.74
15	10.744	0.073	5.00	89.10

3.1. Effect of initial pH

Studies show that one of the most important parameters that should be controlled in Fenton processes to achieve effective removal is the pH of the contaminated solution. But, the operational optimum pH depends on the pollutants in the solution.

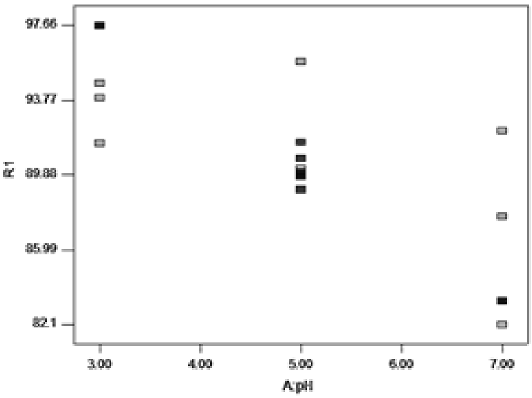

Figure 1. Effect of pH on removal efficiency of Simafix red dye.

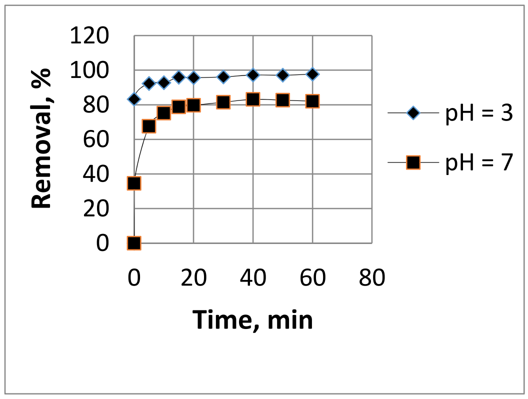

Figure 2. Effect of the initial pH on color removal from textile wastewater at $[Fe^{2+}]$ = 10.744 mM and $[H_2O_2]$ = 0.037mM.

By comparing the removal efficiencies when the values of H_2O_2 and Fe^{2+}concentration at $[Fe^{2+}]$ = 10.744 mM and $[H_2O_2]$ = 0.037 mM. The values of pH were used at pH 3 and pH 7 in the Figure 2. As shown in Figure 1,the highest amount of dye removal is at pH = 3 and the lowest removal is at pH =7. The effect of initial pH of the solution was investigated in acidic solution from pH = 3 to pH = 7 at 20 W UV power. The removal of colour occurred rapidly and reached the maximum point, around 83.30 to -97.67 % after 5 minutes to 60 minutes at the initial pH = 3, the corresponding values at pH = 7 are 34.62 % and 62.09 % as shown in Figure 2. The peak initial pH for treatment of textile wastewater by the Photo-Fenton oxidation process was pH = 3 (Figure 2) and this pH was consistent with some previous works [9],[10],[11]. Igor et al. [9] explained that at pH values were below pH 3 the removal efficiencies were decreased because of the enhanced stability of H_2O_2 and reduced reactivity with ferrous ions. On the other hand, at higher pH than pH 3 precipitated iron in a form of hydroxides is excluded from Fenton catalytic cycle. By checking the order of reactions in Fenton processes, we knew that the date in all runs followed the second – order.

Which experiment conditions that were mentioned above. We checked the second-order for the data of the reactions. From the Figure 3, it is easy to recognize that the rate of reactions at pH = 3 is equal to 10 times of the rate of reactions at pH = 7 (rate are 0.001 and 0.0001). This rate means that at pH = 3 the reaction rate is much faster than pH = 7.

3.2. Effect of initial Fe^{2+} concentration

The effect of Fe^{2+} dosage in the Photo-Fenton oxidation process on the treatment of textile wastewater was investigated under different Fe^{2+} dosages (7.16- 14.32) and under controlled condition (UV power of 20 W) (Table 1). By maintaining the pH = 7; $[H_2O_2]$ = 0.073 mM, the concentration of Fe^{2+} were 7.32 mM and 7.16 mM. The removal efficiencies were showed in the Figure 4 below:

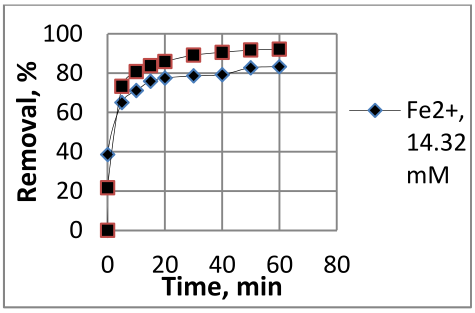

Figure 3. Effect of the initial Fe^{2+} concentration on color removal from textile

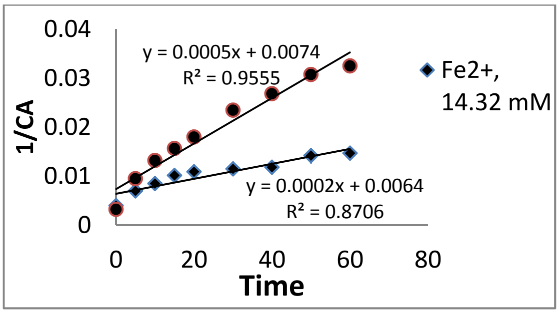

Figure 4. Second – order of reactions in different concentrations of Fe^{2+}.

It can be seen from Figure 3 that the removal efficiencies of Fe^{2+}] = 7.16 mM were always higher than [Fe^{2+}] = 14.32 mM. The removal efficiencies with Fe^{2+}] = 7.16 mM after 5 minutes is 73.27 %, after 60 minutes is 92.19 %; with [Fe^{2+}] = 14.32 mM is 65.02 % and 83.30 % after 5 minutes and 60 minutes. Perhaps the concentration of Fe^{2+} = 7.16 mM is the optimum value or higher than optimum value. Therefore, when the concentrations of Fe^{2+}increase, the removal efficiencies decrease.This suggests that Fe^{2+}goes into a competing reaction and does not merely act as a catalyst hence, it also reacts with HO• (Eq. 3) [3]. Kusic et al. [10] was also recognized that at high Fe^{2+} concentration may be attributed to the pronounced interference of dye spectra and spectra of iron complexes. The maximum removal efficiency at these experiment conditions was not very high (92.19 %) compare to other experiment conditions. It maybe because of other factors (e.g. pH = 7). The influent of Fe^{2+} concentrations to the rate of reaction were illustrated in the Figure 4. Figure 4 showed that the slope of the straight line with [Fe^{2+}] = 7.16 mM is 0.0005 which is higher than the slope of the straight line with [Fe^{2+}] = 14.32 mM is 0.0002. It meant that the reactions of [Fe^{2+}] = 7.16 mM happened faster than the [Fe^{2+}] = 14.32. This result demonstrated for the removal efficiencies mentioned in Fig.3.

3.3. Effect of initial H_2O_2 concentration

When the concentration values of H_2O_2 is changed between 0.037 and 0.011 mM; the values of pH = 5;[Fe^{2+}] = 14.32 mM are constant. The results are showed in the Figure 6

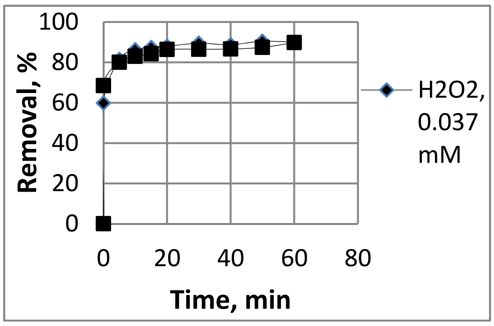

Figure 5. Effect of the initial H_2O_2 concentrationon color removal from textile wastewater at pH = 5; [Fe^{2+}] = 14.32 mM.

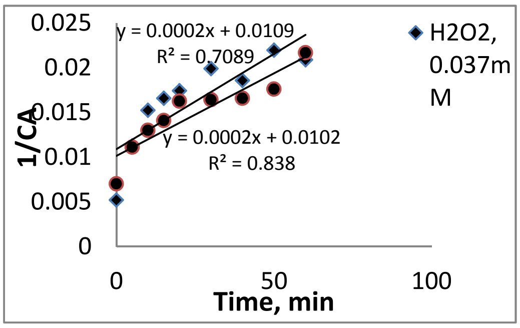

Figure 6. Second – order of reactions in different concentration of H_2O_2.

For the concentration range of H_2O_2 studied between 0.037 mM and 0.11 mM(20 W of UV power). There is a slight differences in color removal as shown in Fig. 5. At $[H_2O_2]$ = 0.037 mM the removal efficiencies are 81 % at after 5 minutes and it reached 90 % after 60 minutes; for $[H_2O_2]$ = 0.11 mM the removal efficiencies are 80 % to 90 % after 5 minutes to 90 minutes. From previous studies [11], a very high concentration of H_2O_2 lead to in a decreased reduction because the HO• produced will be scavenged by this H_2O_2 as in (Eq.2). There is a threshold concentration where there is no increase in removal when increasing the H_2O_2 concentration. More than the optimum condition, it was observed that there is a slight or no degradation occurs. The second-order for the reactions with the same values of pH and Fe^{2+} concentration but different values of H_2O_2 concentration were checked. Figure 6 showed that the rate of reactions when the H_2O_2 concentrations were 0.037 mM and 0.11 mM were the same (0.002). It could be conclused that the H_2O_2 concentrations (0.037 mM and 0.11 mM) are not very different enough to have much effect in removal efficiencies and the reaction rate.

3.4. Effect of UV exposure

By doing the two experiments with the conditions: pH = 7; $[Fe^{2+}]$ = 10.744 mM; $[H_2O_2]$ = 0.0.11 mM. The first one was done with UV, the second one was performed without UV.

Figure 7 displayed the removal color as a function of UV power in the 60 minutes. From above figure we see that after 15 minutes the removal efficiency of the reactor with UV started to increase faster than the one without UV. Perhaps after 15 minutes the UV can make the effect to enhance producing hydroxyl radical. In the absence of UV power, the color removal was 83.57 %. As the UV power exposure increased, the removal of color increased slightly. At this condition, the removalcolor was around 87.32 %. Using the UV power only resulted in slight different color removal. This may be caused by the initial pH = 7, which results to lower removal efficiency relative to the initial pH = 3.

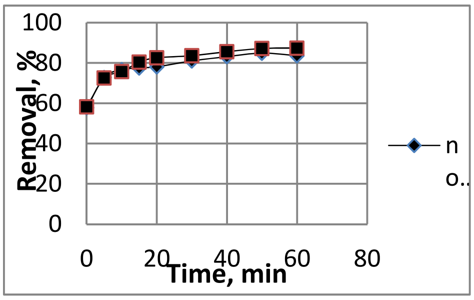

Figure 7. Effect of UV on color removal in wastewater within 1 hour at the

3.5. Optimization of Photo-Fenton Using BBD

The main purpose of wastewater treatment are high removal efficiency and low cost. Based on the results of the experiment which were mentioned above we know that the optimum value of pH for Fenton processes is pH = 3. By minimum values of Fe^{2+}(7.162 mM) and H_2O_2 (0.037 mM) concentrations in order to achieve the low cost in treating. Using the design expert program we get the predict optimum values removal efficiencies with the different experiment conditions which are tabulated in the Table 2.

Table 2. Prediction the removal efficiency with different optimum values.

Solutions No.	pH	H_2O_2	Fe^{2+}	R_1	Desirability
1	3.00	1.00	200.00	95.8184	0.959
2	3.03	1.00	200.00	95.7652	0.957
3	3.00	1.00	200.90	95.8039	0.956
4	3.05	1.00	200.00	95.7251	0.955
5	3.00	1.03	200.00	95.825	0.951
6	3.00	1.05	200.00	95.8278	0.946
7	3.17	1.00	200.00	95.4685	0.944
8	3.23	1.00	200.00	95.3499	0.943
9	3.27	1.00	200.00	95.2685	0.941
10	3.00	1.12	200.08	95.8406	0.934
11	3.45	1.00	200.00	94.914	0.932
12	3.51	1.00	200.00	94.7902	0.926
13	3.00	1.16	200.39	95.8422	0.866
14	3.37	1.07	200.00	95.0838	0.897
15	3.00	1.07	214.68	95.5922	0.814

Aside from fitting a model for color removal, initial rate was also included as a response to predict the efficiency of the process at optimum conditions. In order to check the significant of the prediction values from the prediction table we repeated the first two solution number. For the first one the prediction removal efficiency if R = 95.8184 %, the actual value was achieved from experiment is R = 95.6592 % (significant 99 %). For the second predicted values R = 95.7652, the actual value is R = 95.6528 (significant 99.9 %). These means the predicted values are close with the actual values. Therefore, we can use the predicted values in the table to apply in the actual wastewater treatment.

4. CONCLUSION

This study applied Box-Behnken design in optimizing the Photo-Fenton process on the degradation of dye (Simafix).The results showed that all of the reactions in removing simafix red dye by fenton process follow second-order. When we increased the concentration of Fe^{2+} from 7.162 mM to 14.162 mM, the removal efficiencies decreased. When we increased the H_2O_2 concentration from 0.037 mM to 0.11 mM the removal efficiencies slightly decreased. The optimum value of pH is pH = 3. By in range pH value and minimum the concentration of Fe^{2+} and H_2O_2 we can get 15 solutions numbers for the optimum values.

Acknowledgement: I would like to express our sincere gratitude, profound appreciation, and deepest thanks to Hochiminh City University of Natural Resources and Environment for financial support.

REFERENCES

1. Sheng H. L., Ming L. C. - Purification of textile wastewater effluents by a combined Fentonprocess and ion exchange. Desalination **109** (1997) 121-130.
2. Sanja P., Dinko V., Natalija K., Danijel S. - Decolourization and mineralization of commercial reactive dyes by using homogeneous and heterogeneous Fenton and UV/Fenton processes, Journal of Hazardous Materials **164** (2009) 1137–1145.
3. Shyh F. K., Chih H. L., Shei T. P. - Decolonization of textile wastewater by photo-Fenton oxidation technology. Chemosphere **41** (2000) 1287-1294.
4. Carmen S.D. R., Luis M. M., Rui A.R. B. - Treatment of textile effluent by chemical (Fenton's Reagent) andbiological (sequencing batch reactor) oxidation. Journal of Hazardous Materials **172** (2009) 1551–1559.
5. Taha M. E., Yasser M. R., Zeinhom H. M., Hassan M.H. Abd El B. - Decolorization of Mordant red 73 azo dye in water using H2O2/UV and photo-Fenton treatment. journal of Hazardous Materials **174** (2010) 352–358.
6. Jian-Hui S., Sheng-Peng S., Guo-Liang W., Li-Ping Q. - Degradation of azo dye Amido black 10B in aqueous solution by Fenton oxidation process. Dyes and Pigments **74** (2007) 647e652.
7. IdilA., IsilAkmehmetB., Detlef W. B. - Advanced chemical oxidation of reactive dyes in simulateddyehouse effluents by ferrioxalate-Fenton/UV-A and TiO2/UV-A processes. Dyes and Pigments **47** (2000) 207±218.
8. Papadopoulos A.E., Fatta D., Loizidou M. - Development and optimization of dark Fenton oxidation for thetreatment of textile wastewaters with high organic load. Journal of Hazardous Materials **146** (2007) 558–563.
9. Igor T. P., NatalijaK. at al. - Comparative study of UV/TiO2, UV/ZnO and photo-Fenton processesfor the organic reactive dye degradation in aqueous solution. Journal of Hazardous Materials **148** (2007) 477–484.
10. Kusic H., NatalijaK., LidijaS. - Azo dye degradation using Fenton type processes assisted byUV irradiation: A kinetic study. Journal of Photochemistry and Photobiology A: Chemistry **181** (2006) 195–202.
11. Ting, W.-P, Lu, M.-C & Huang Y.-H(2009). Kinetics of 2,6- dimethylanine degradation by electro-Fenton process, Journal of Hazardous Materials **161** (2-3), 1484-1490.