Treatment of Textile Dyeing Wastewater by Photo Oxidation using UV/H$_2$O$_2$/Fe^{2+} Reagents

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ABSTRACT: Treatment of textile wastewater was carried out at room temperature in a batch reactor by using the Photo-Fenton oxidation process. The effects of initial pH of the solution (pH = 1-7), ferrous ion concentration (0-100 mg×l^{-1}) and UV power (0-120 W) on chemical oxygen demand (COD) and color removal were examined. The results showed that this process was enhanced at the acidic pH range. The optimum condition was found to be at pH = 3, 80 mg Fe^{2+}×l^{-1}, 5-10 minutes operating time, 60 W UV power and 200 mg H$_2$O$_2$×l^{-1}. At this condition, approximately 52% and 90% of COD and color were removed, respectively. During the treatment process, a small amount of sludge (5.8×10^{-5} kg×kg COD^{-1}) was generated. The presence of heterogeneous photocatalyst such as TiO$_2$ in the system accelerated the removal percentage of COD and color.

KEYWORDS: Textile wastewater treatment, Photo-Fenton process, Decolorization.
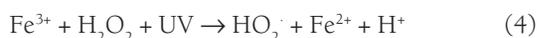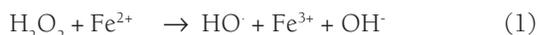
INTRODUCTION

Textile industry demands a large amount of process water (21-377 m^3×tons^{-1} of textile)[1] and generates large quantities of wastewater from various steps of dyeing processes. The textile wastewater is characterized by high content of dyestuff, salts, high COD deriving from additives, suspended solid (SS) and fluctuating pH depending on the process. The conventional process used to treat wastewater from textile industry is chemical precipitation with alum or ferrous sulfate. The drawbacks of this process are the generation of a large volume of sludge leading to the disposal problem, the contamination of chemical substances in the treated wastewater, and etc. For a more practical application, different processes were developed to treat wastewater from textile industry such as filtration process[2], biological process[3-5], adsorption process[6-8], electrochemical process[9-11], and ozone process[12], etc.

The processes of advanced oxidation (AOP), involving corona discharge process (CDP), hydrogen peroxide (H$_2$O$_2$), ozone (O$_3$), and/or Fenton reagent, both with or without a source of UV light, have been investigated for many years in numerous research centers due to their high reactivity but low selectivity. The mechanism of chain reactions involves hydroxyl (OH$^·$) and hydroperoxy radicals (HO$_2^·$). The main advantages of this method include the redu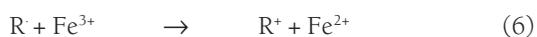ction of by-product generation, absence of kinetic limitations, generation of highly reactive free radicals, elimination of overdosing hazardous oxidizing agents, and high process rate and efficiency.[13-14] H$_2$O$_2$/UV-Vis photo-oxidation process was used to treat waterborne substances in a flow stirred tank reactor and a tubular flow reactor.[15] The results indicated that a flow stirred tank reactor was more effective than a tubular one, and the rate controlling variable in the system was the photon flux. The Fenton process (H$_2$O$_2$/Fe^{2+}) was well represented by the 1st order reaction kinetics. The reaction rate was strongly dependent on temperature, H$_2$O$_2$ and FeSO$_4$ dosages.[16] Compared with other conventional processes such as electrochemical oxidation, ozone oxidation or hypochlorite oxidation, the Fenton process was more effective.[17] Kang and Chen[18] demonstrated that the Fenton process was suitable to be used as a decolorization agent, whereas the COD was primarily removed by Fenton coagulation rather than by Fenton oxidation. The combination of the corona discharge and the Fenton processes can achieve decolorization and degradation of dye stuff up to 100 and 98%, respectively[19]. Introduction of UV source into the Fenton process called Photo-Fenton can provide the decolorization of textile process.[20] The removal of color can be divided into three stages; (1) fast color removal for the first 5 min by H$_2$O$_2$/Fe^{2+} process, (2) slow removal at time between 5 and 30 min attributed by H$_2$O$_2$/UV process, and (3) color resurgence by photoreduction of ferric ion. The kinetics

of COD and color removal were consistent with those of H_2O_2 and Fe^{2+} dosage, respectively. Higher dosage of Fe^{2+} was found to be significant on the initial removal rate of COD whereas the color was favorably removed by increasing UV power.[21]

The reactivity and efficiency of the Photo-Fenton oxidation process strongly depend on the formation of $OH^.$ radicals, whose main formation reactions consist of Fenton reaction, photolysis of hydrogen peroxide and photoreduction of ferric ion as the following reactions.[22-23]

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

$$H_2O_2 + UV \rightarrow 2HO^. \qquad (2)$$

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

$$Fe^{3+} + H_2O_2 + UV \rightarrow HO_2^. + Fe^{2+} + H^+ \qquad (4)$$

Reaction (1) takes place both in the presence and absence of light, and the concentration of Fe^{2+} is low as long as there is sufficient H_2O_2 in the reactor. The amount of $OH^.$ radical in reaction (2) is efficiently produced under acidic condition whereas the $H_2O_2/$ UV process according to reaction (3) is independent of pH condition. Reaction (4) is the ferric ions-catalyzed decomposition of H_2O_2, which is then followed by heat- or UV-induced formation of ferrous ions and perhydroxyl radical. The rate constant of reaction (1) was reported to be about 2,650 times larger than that of reaction (4).[24] The $OH^.$ radicals formed are capable of oxidizing the organic pollutants (RH), thus causing the chemical decomposition of these compounds as expressed by reactions (5)-(7).

$$HO^. + RH \rightarrow H_2O + R^. \qquad (5)$$

$$R^. + Fe^{3+} \rightarrow R^+ + Fe^{2+} \qquad (6)$$

$$R^+ + H_2O \rightarrow ROH + H^+ \qquad (7)$$

Instead of using synthetic wastewater as in many previous works, the treatment of real wastewater from a textile plant was carried out here by using the photo oxidation process. Effects of initial pH, dosage of Fe^{2+}, UV power and dosages of H_2O_2 on the COD and color removal were investigated in a batch reactor at room temperature (approximately 30 $^{\circ}$C).

MATERIALS AND METHODS

Wastewater samples containing acid dye from a textile plant in Thailand were used in this study (Table 1). In each batch, a glass jar filled with 1 litre of wastewater

Table 1. Characteristics of textile wastewater.

| Characteristics	Value
COD ($mg \times l^{-1}$)	6,500-27,000
BOD ($mg \times l^{-1}$)	8,500-10,000
Color (Pt-Co unit)	1,584-2,310
pH	6.68-8.36
Conductivity ($mS \times cm^{-1}$)	1.74-2.63
Turbidity (NTU)	105-164
Other compounds (Na_2CO_3, Cr, Fe, formaldehyde, NaOH, etc.)	

placed in the middle of the UV-protected box having a dimension of $0.68 \times 0.68 \times 0.78$ m^3 and surrounded by 8 UV lamps ($\lambda = 365$ nm, 15 W) as shown in Figure 1. The solution was agitated by using a stirrer at 420 rpm to achieve a complete mixing. As the experiment progressed, 20 ml of sample were collected at different time intervals to measure the COD and color. Prior to chemical analysis, the sample was adjusted to pH value above 11 by using 12 M NaOH to terminate the reaction and then readjusted to pH value of 4. The COD or other wastewater properties and color were analyzed according to the standard procedures described previously[25] and by using UV/Vis spectrophotometer (Jasco V-520), respectively. For all experiments, the operating time was fixed at 60 minutes. The data reported in this experiment were the average values obtained from the duplicate of experiments and the acceptable error in this work was 3%.
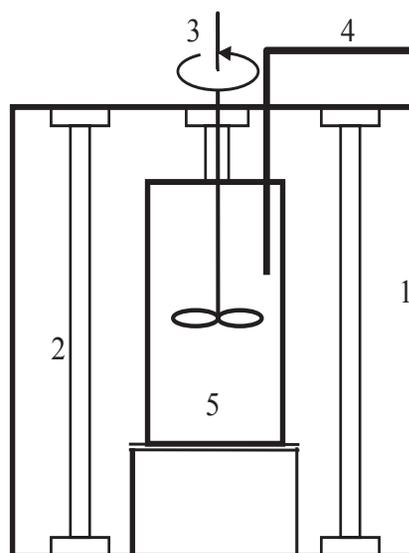
Fig 1. Experimental set up of the Photo-Fenton oxidation process: 1. UV box 2. UV lamp 3. Stirrer 4. Sample port and 5. Reactor.

RESULTS AND DISCUSSION

The effect of initial pH of the solution was investigated in acidic solution from pH = 1 to pH = 7 with 100 mg $H_2O_2 \times l^{-1}$, 20 mg $Fe^{2+} \times l^{-1}$, 60 W UV power. The removal of color occurred rapidly and reached the maximum point, around 78-83%, at the initial pH = 3-5 within 5 minutes as shown in Figure 2, and remained constant when the operating time proceeded.
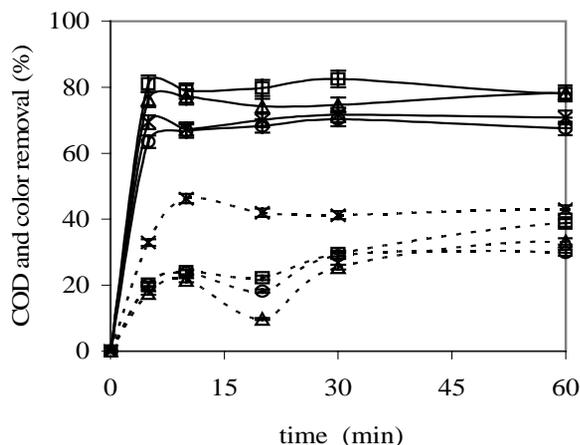
Fig 2. Effect of the initial pH on the COD and color removal from textile wastewater: pH = 1 (×), pH = 3 ( ), pH = 5 (△), pH = 7 (O): Color (——), COD (······).

On the contrary, the COD reached the maximum removal, around 20-38%, within 5-10 minutes at the initial pH between 1 and 3 and remained constant after 20 minutes. In neutral condition (pH = 7), the removal percentage was reduced because the generation of $OH^.$ had considerably slowed down due to the decomposition of H_2O_2 to H_2O and O_2. In order to remove the COD and color simultaneously, the optimum
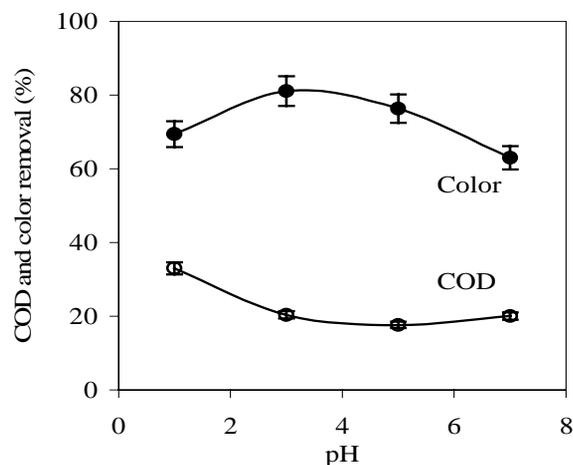
initial pH for treatment of textile wastewater by the Photo-Fenton oxidation process was pH = 3 (Figure 3) and this pH was consistent with some previous works.[26]

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 (0-100 mg×l^{-1}) and under controlled condition (100 mg $H_2O_2 \times l^{-1}$, UV power of 60 W, pH = 3). The sharp removal of COD and color was observed in the first 5-10 minutes and remained constant as the operating time proceeded as shown in Figure 4.
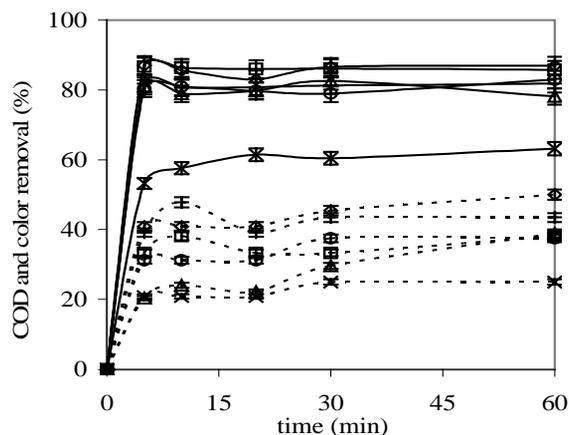
Fig 4. Effect of Fe^{2+} on the COD and color removal from textile wastewater. Fe^{2+} = 0 mg×l^{-1} (×); Fe^{2+} = 20 mg×l^{-1} (△); Fe^{2+} = 40 mg×l^{-1} (O); Fe^{2+} = 60 mg×l^{-1} ( ); Fe^{2+} = 80 mg×l^{-1} (◇); Fe^{2+} = 100 mg×l^{-1} (+): Color (——), COD (······).
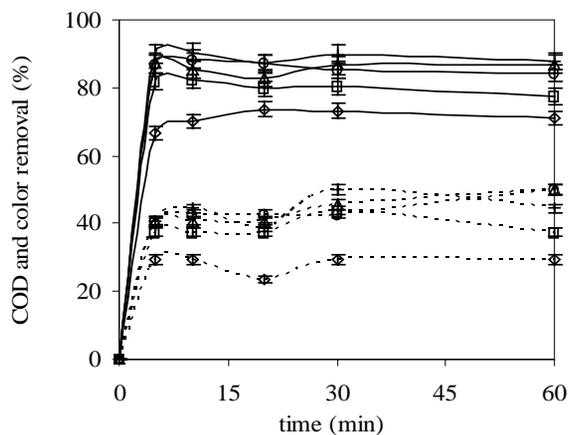
Figure 5 shows the removal of COD and color from textile wastewater measured within 5 minutes of operating time. The results indicated that without Fe^{2+}, the removal of color and COD was 53 and 20%, respectively. The increase of Fe^{2+} dosage significantly

Fig 3. Effect of the initial pH on the COD and color removal from textile wastewater within 5 minutes of operating time.
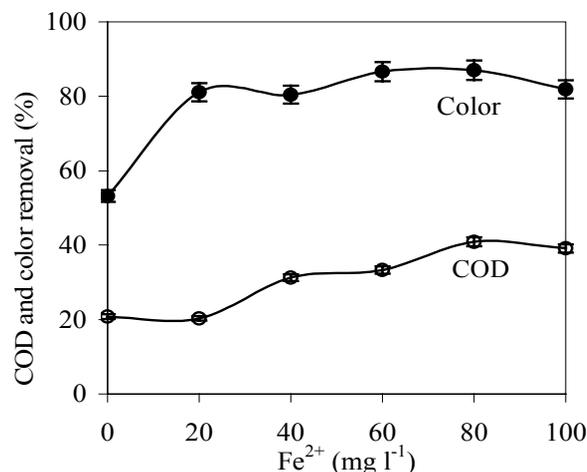
Fig 5. Effect of Fe^{2+} on the COD and color removal from textile wastewater within 5 minutes of operating time.

affected the color removal but only slightly affected the COD removal. The removal of color required relatively low Fe^{2+} dosages. However, much higher dosages of Fe^{2+} are necessary to obtain a high level of COD removal because a large amount of Fe^{2+} can promote the formation of OH^- through the Fenton reaction as shown by reaction (1). To treat the COD and color simultaneously, the optimum Fe^{2+} dosage was 80 mg×l⁻¹. At this condition, the removal of COD and color was 41 and 87 %, respectively.

The effect of UV light was explored at different UV powers ranging from 0-120 W under the controlled condition of 80 mg Fe^{2+}×l⁻¹, 100 mg H_2O_2×l⁻¹, and pH = 3. The results shown in Figure 6 indicated that the removal of COD was strongly observed in the first 5 minutes (30-42%) and remained constant after 10 minutes, while the color removal of 68-90% progressed rapidly within 5-7 minutes.
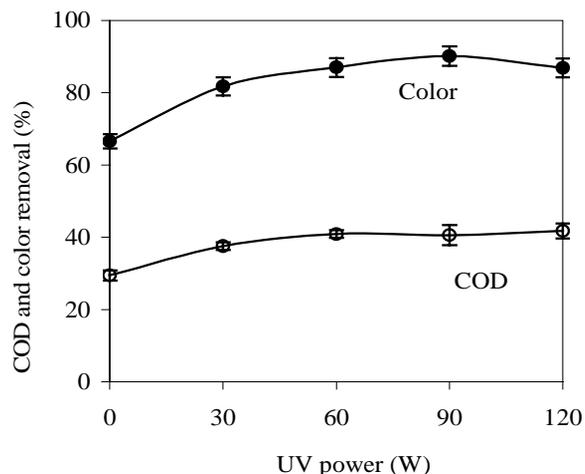

Fig 6. Effect of UV power on the COD and color removal from textile wastewater: UV = 0 W (◇), UV = 30 W ( ), UV = 60 W (△), UV = 90 W (+), UV = 120 W (O): Color (——), COD (······).

Figure 7 displays the removal of COD and color as a function of UV power in the first 5 minutes. In the absence of UV power, the removal of COD and color was 30% and 67%, respectively. As the UV power increased, the removal of color increased slightly whereas that of COD did not change. From the curve, to remove COD and color simultaneously, the optimum UV power used was 60 W. At this condition, the removal of COD and color was around 41% and 87%, respectively. Using the higher UV power only resulted in slight different COD and color removal.

According to above results, it seems that the amount of H_2O_2 was not enough to remove the COD in wastewater to a level greater than 41%. Figure 8 displayed the removal percentage of the COD and color at different H_2O_2 dosages by using 80 mg Fe^{2+}×l⁻¹, 60 W, and initial pH of 3. As the

H_2O_2 dosages increased from 100 to 300 mg×l⁻¹, the removal percentage of color increased very slightly from 87% to 91% whereas that of COD increased from 41% and reached its maximum removal percentages of 52% at H_2O_2 dosages of 200 mg×l⁻¹. Excess H_2O_2 could not achieve a higher percentage of COD removal. Furthermore, it can interfere the measurement of COD.[18] In addition, the cost of H_2O_2 is expensive (approximately 22.25 US$/liter, Ajax). Therefore, in actual operation, the dosage of H_2O_2 should be minimized.

Fig 7. Effect of UV power on the COD and color removal from textile wastewater.
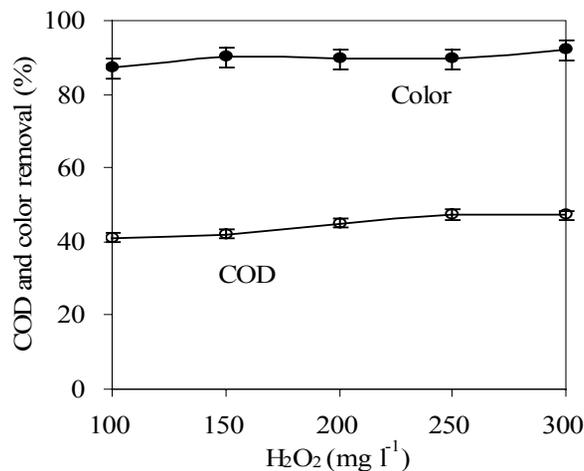
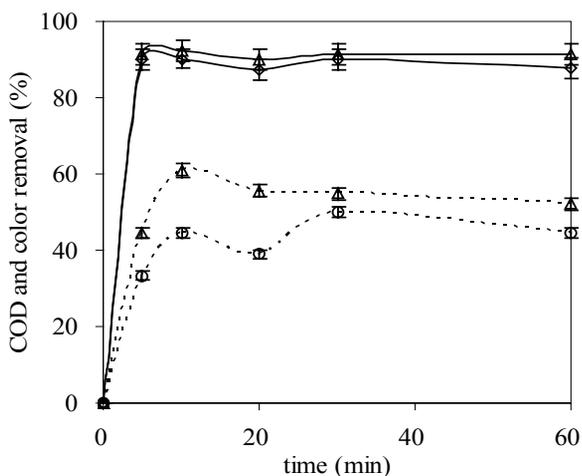**Fig 8.** Effect of H_2O_2 on the COD and color removal from textile wastewater.

In order to get a higher percentage of COD and color removal, a large quantity of OH^- radicals in the system should be produced. One way to produce the OH^- radicals is the utilization of heterogeneous photocatalyst. In this study, TiO_2 was considered as a candidate catalyst because it can accelerate the reaction

according to the following reactions.[27]

$$TiO_2 + UV \quad \rightarrow \quad TiO_2(e^- + h^+) \tag{8}$$

$$TiO_2(e^-) + H_2O_2 \quad \rightarrow \quad TiO_2 + OH^- + OH^- \tag{9}$$

$$TiO_2(h^+) + OH^- \quad \rightarrow \quad TiO_2 + OH^- \tag{10}$$

Figure 9 shows the results of the COD and color removal in the presence and absence of TiO_2 by using $100\ mg \times l^{-1}\ H_2O_2$, $80\ mg \times l^{-1}\ Fe^{2+}$, UV power = 90 W and initial pH = 3. For both with and without TiO_2, the very rapid removal of COD and color was observed within the first 5-10 minutes. During this time, in the absence of TiO_2, the removal of COD and color was 44% and 90%, respectively. On the other hand, with TiO_2 (7.99 g/l), the COD and color were removed respectively around 61% and 92%. The results indicated that the presence of TiO_2 could promote the COD removal by about 20%. It had, however, a slight effect on color removal.

Fig 9. Effect of TiO_2 on the COD and color removal as a function of time. with TiO_2 ($\triangle$); without TiO_2 (O): Color (—), COD (·····).

Figure 10 shows the example of textile wastewater before and after treatment by the Photo-Fenton oxidation process. The color of wastewater after treatment is clear and not objectionable in comparison with that before treatment. When the treatment process finished, a small amount of sludge was generated ($5.8 \times 10^{-5}\ kg \times kg\ COD^{-1}$) compared with the conventional anaerobic process ($0.611 \pm 0.33\ kg \times kg\ COD^{-1}$).[28] This sludge was the $Fe(OH)_3$ occurring during the process. The cost of this treatment process was not estimated because this work was carried out as a batch-mode reaction at a bench-scale. So, it is difficult to estimate the real treatment cost in this situation.

In addition, in order to apply this process to textile industry, a proper design of continuous process in a pilot-scale experiment should be attained.
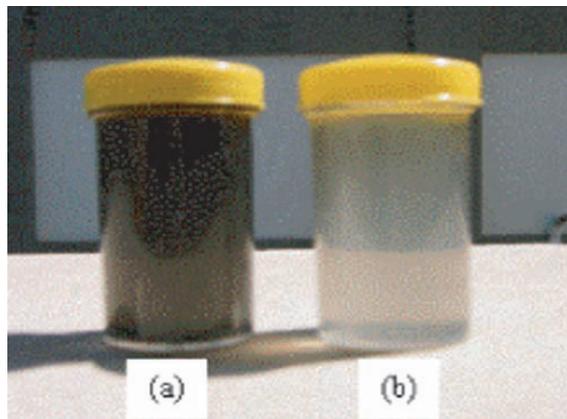
Fig 10. Textile wastewater (a) before and (b) after treatment by the Photo-Fenton oxidation process.

CONCLUSIONS

The author attempted to remove the COD and color from textile wastewater by employing the Photo-Fenton oxidation process in a batch reactor. The results indicated that the COD and color was fast removed during the first 5-10 minutes and they can reborn at very long operating time due to photoreduction of ferric ion in the system. To remove the COD and color simultaneously, the optimum condition in this study was found to be at $80\ mg\ Fe^{2+} \times l^{-1}$, UV power = 60 W, initial pH = 3, $200\ mg\ H_2O_2 \times l^{-1}$ and 5-10 minutes operating time. At this condition, approximately 52% and 90% of the COD and color were respectively removed. Using a heterogeneous catalyst such as TiO_2 can expedite the removal of COD and color in textile wastewater, and it can be reused in the system by using a simple filtration. By employing the Photo-Fenton oxidation process, it was found that this process was more suitable for color removal than COD removal.

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