

The optimization of the photo-oxidation parameters to remediate wastewater from the textile dyeing industry in a continuous stirred tank reactor

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Abstract—The remediation of textile dyeing wastewater was carried out at ambient temperatures in a pilot-scale continuous stirred tank reactor by using the photo-Fenton oxidation process. The preliminary results suggest that the treatment system reached a steady state condition within 5-10 min after it was started up. By using a 2^k factorial design, the effects of various parameters on the removal efficiency of color, BOD and COD were identified under steady state conditions. The removal efficiencies of color and BOD were affected by the feed rate of H_2O_2 and Fe^{2+} , whereas none of the parameters in the investigated ranges affected the removal efficiency of COD. Consequently, using univariate analysis to investigate higher parameter range values, the optimum conditions for treating textile wastewater were found to be 25 ml H_2O_2 /min, 5 ml Fe^{2+} /min and 90 W UV-A power for 20 min. In addition, the removal of all pollutants was enhanced within the acidic pH range. Approximately 69.2, 99.4 and 48.5% of color, BOD and COD were removed, respectively. However, the concentration of TDS increased slightly during the treatment period due to the formation of new species or intermediate oxidation products. Nevertheless, all values of pollutants in the treated wastewater except COD were in the range of the standard values permitted for discharge into the environment.

Key words: Textile Wastewater, Photo-Fenton Process, Remediation, Continuous Stirred Tank Reactor, Advance Oxidation

INTRODUCTION

Approximately 200-2,000 m³/day of water is required for the dyeing steps in the textile process, leading to the generation of a large quantity of wastewater, and this is true for each of the different steps of the dyeing processes [1]. The resultant wastewater is characterized by high content of dyestuff, salts, a high chemical oxygen demand (COD) derived from additives, a high suspended solid (SS) content and a fluctuating pH, depending on the process used. The conventional process used to treat such wastewater from the textile industry is based upon chemical precipitation with alum or ferrous sulfate, but the drawback is the generation of large volumes of environmentally toxic sludge leading to disposal problems, contamination of chemical substances in the treated wastewater, etc. For more practical application, a diverse array of different processes have been developed to treat textile industry wastewater including processes based upon filtration [2], biological [3-5], adsorption [6-8], electrochemical [9-11] and ozone [12].

The processes of advanced oxidation (AOP) involving corona discharge process (CDP), hydrogen peroxide (H_2O_2), ozone (O_3), or/and 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. They share in common the mechanism that the chain reactions involve hydroxyl (OH^\bullet) and hydroperoxy radicals (HO_2^\bullet). The main advantages of this approach include the reduced generation of by-products, absence

of kinetic limitations, generation of highly reactive but unstable (short lived) free radicals with the elimination of overdosing hazardous oxidizing agents, and a high process rate and efficiency [13,14]. The H_2O_2 /UV-Vis photo-oxidation process was found to be more efficient in a feed stirred tank reactor than a tubular feed reactor to treat waterborne substances with the rate-controlling variable in the system being photon flux [15]. The Fenton process ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) is well established as following first order rate reaction kinetics and is strongly dependent on the temperature, H_2O_2 and FeSO_4 dosages [16]. Compared with other conventional processes including electrochemical, ozone or hypochlorite oxidation, the Fenton process is more effective [17]. Moreover, the Fenton process is suitable as a decolorization agent, whereas the COD was primarily removed by Fenton coagulation rather than by Fenton oxidation [18]. The combination of corona discharge and Fenton processes can achieve the decolorization and degradation of dyes by up to 100 and 98%, respectively [19]. The introduction of a UV-A source into the Fenton process, the so-called photo-Fenton process, can provide the decolorization [19], and can be divided into three stages: (1) fast color removal for the first 5 min by $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ process, (2) slow removal at 5 to 30 min attributed to the H_2O_2 /UV-A process, and (3) color resurgence by photoreduction of ferric ions. The kinetics of COD and color removal were consistent with those of H_2O_2 and Fe^{2+} dosage, respectively. A higher dose of Fe^{2+} was found to be significant for the initial removal rate of COD, whereas the color was favorably removed by increasing the UV power [20]. The reactivity and efficiency of the photo-Fenton oxidation process, however, depends strongly on the formation of OH^\bullet radicals, which are mainly formed from the Fenton reaction, photolysis of hydrogen peroxide and pho-

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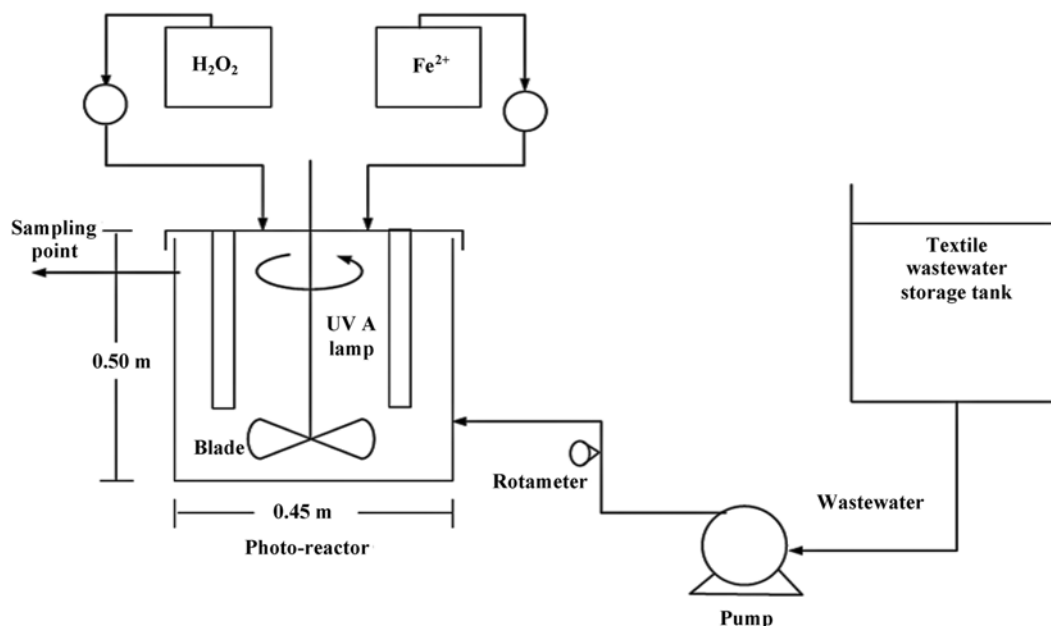
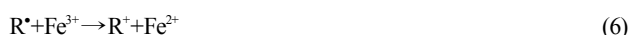


Fig. 1. Experimental set up of the continuous flow photo-Fenton oxidation process.

to reduction of ferric ions as summarized in reactions (1)-(7) below [21].



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^\bullet radical in reaction (2) is efficiently produced under acidic conditions, whereas the $\text{H}_2\text{O}_2/\text{UV}$ process (Reaction 3) is independent of the pH. The ferric ion-catalyzed decomposition of H_2O_2 (4), which is followed by heat- or UV-induced formation of ferrous ions and perhydroxyl radical, has a rate constant some 2,650 times smaller than that of reaction (1) and is limiting [22]. The OH^\bullet formed is capable of oxidizing the organic pollutants (RH) causing their chemical decomposition (Reactions (5)-(7)). Besides the above reactions, the ferrous ion generated can also react with OH^\bullet leading to the formation of ferric hydroxo complexes, which become coagulation species with dye molecules and/or other dissolved suspended solids which are captured and precipitated out from the wastewater within the pH range 3-7 [16].

In this report, instead of using synthetic wastewater in a batch reactor as in many previous works, the actual wastewater from a textile plant was treated by using photo-oxidation with UV/ H_2O_2 / Fe^{2+} reagent in a continuous stirred tank reactor. The influence of several parameters on the removal of color, biological oxygen demand (BOD) and chemical oxygen demand (COD) was examined

at ambient temperature (approximately 30 °C), and the experiment was designed by using a 2^k factorial design together with the univariate method.

MATERIALS AND METHODS

Actual textile wastewater containing either acid dye or disperse dye from a textile plant in Thailand was used in this study. The experimental setup, schematically shown in Fig. 1, consisted of a 150 liter wastewater storage tank and a photo-reactor. The photo-reactor was constructed by using a stainless steel cylinder with 0.45 m diameter and 0.5 m height. Inside this reactor, glass tubes (Duran) contained the UV-A lamps ($\lambda=365$ nm, 15 W each). Due to the variation in the textile wastewater properties between samples, as summarized in Table 1, in each experiment homogeneity of wastewater was first attained by pumping wastewater from the textile plant reservoir to the storage tank of the treatment process, and stirring using the motor stirrer. Subsequently, the homogenized wastewater was fed into the photo-reactor by using the rotary pump (Panworld, NH-50PX) with a constant feed rate of 4 l/min. The capacity of wastewater inside the reactor was maintained constant at approximately 60 liters leading to a retention time of 8.75 min. At the same time, the required volume of 0.1 M Fe^{2+} (prepared from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, Univer) and H_2O_2 (30% (w/v), Univer) was supplied into the reaction tank by a peristaltic pump (Cole-Parmer, U-07554-95) at the preferable feed rate. As the experiment proceeded, 120 ml of sample was collected at different time intervals to measure color, BOD, COD and total dissolved solid (TDS). Prior to chemical analysis, the sample was adjusted to pH 11 (or slightly above) by addition of 12 M NaOH to terminate the reaction, and then readjusted to pH 4 by H_2SO_4 [23]. The COD and other wastewater properties and color were analyzed according to the procedures described in standard methods [24] and by using a UV/Vis spectrophotometer (Jasco V-530) at a wavelength of 465 nm.

Table 1. Characteristics of textile wastewater

Characteristics	Thai standard	Properties of wastewater	
		Before treatment	After treatment
pH	5.5-9.0	7.21-8.03	6.69-8.70
BOD (mg/l)	≤60	400-2,250	<30
COD (mg/l)	≤400	3,360-28,800	1,600 - 1,760
TDS (mg/l)	≤3,000	1,488-5,168	1,572-1,600
Conductivity (mS/cm)	NA	3.56-4.72	NA
Color (Pt-Co unit)	Not objectionable	1,001-3,230	Not objectionable
Turbidity (NTU)	NA	105-164	NA
Iron ions (mg/l)	NA	NA	<13

Table 2. Predictor variables and their coded levels and actual value used for experimental design

Variable	Symbol	Real value of coded levels		
		-1	0	+1
H ₂ O ₂	x _A	5	15	25
Fe ²⁺	x _B	0	2.5	5
UV-A power	x _C	0	30	60

RESULTS AND DISCUSSION

1. Steady State Time of Pollutant Removal in Continuous Process

The steady state time for pollution removal from actual textile dyeing wastewater was evaluated in a continuous treatment process using the photo-oxidation process with UV/H₂O₂/Fe²⁺ reagents. The experiments were performed at various conditions with the feed rates of H₂O₂, Fe²⁺ and UV-A power as demonstrated in Table 2 and a retention time and initial pH of wastewater in the photo-reactor of 8.75 min and approximately 7, respectively. The results demonstrated that the removal of color for all conditions occurred rapidly within the first 5 min after the start-up time and reached or almost reached its plateau within 10 min operating time as displayed in Fig. 2(a). The maximum color removal (~40%) was observed with either condition VIII (25 ml H₂O₂/min, 5 ml Fe²⁺/min and 60 W UV power) or condition IV (25 ml H₂O₂/min and 5 ml Fe²⁺/min). The presence of UV-A power in the studied range had no apparent effect on the removal efficiency of color. Likewise, similar to color, close to 81% of BOD was removed rapidly within the first 5 or 10 min and reached or almost reached its plateau within 10 min (Fig. 2(b)). Condition VIII (25 ml H₂O₂/min, 5 ml Fe²⁺/min and 60 W UV power), condition IV (25 ml H₂O₂/min, 5 ml Fe²⁺/min) and condition VI (25 ml H₂O₂/min and 60 W UV power) provided nearly similar efficiency of BOD removal, suggesting that the feed rate of Fe²⁺ as well as the UV power appeared to be insignificant within the tested ranges in BOD removal. For COD removal (Fig. 2(c)), in all conditions, COD was reduced slowly and weakly, attaining only an approximate 10-21 and 10-30% reduction within 5-10 and 30 min, respectively.

Thus, under these different operating conditions, although the effects of each parameter on the removal efficiency of color, BOD and COD are still not clear, these preliminary results indicate that the photo-oxidation process in this continuous reactor reached the

steady state condition within 5-10 min, which is similar to the reported photo-oxidation process of synthetic textile wastewater in a batch reactor [25].

2. Regression Model and Analysis of Variance (ANOVA)

To investigate the effects and interactions of all the parameters on the removal efficiency of color, BOD and COD, a 2^k factorial design with the computer program known as Design-Expert 6.0.10 version was conducted with two replications and three center points (Table 3) and analyzed by using a critical value of F₀ (F_{0.05,1,8})=5.59 for a 95% confidence level [26].

According to the ANOVA results of color removal (Table 4), it was found that the F₀ value of parameters H₂O₂, Fe²⁺ and both factors together were higher than the critical F₀ value, supporting that the feed rate of H₂O₂ and Fe²⁺ and interaction of both of them had a significant influence on the efficiency of color removal. The regression model can be expressed by a linear Eq. (8) with a high coefficient of determination (R²) of 0.9261 and with randomly distributed residuals suggesting that the regression model validly represents the experimental data. From this equation, increasing feed rates of only H₂O₂ or Fe²⁺ or both of them led to the increased of color removal. With respect to BOD removal, the feed rate of H₂O₂ and Fe²⁺ also both appeared to significantly affect the BOD removal efficiency, but in contrast to color this was without any significant interaction between the two variables. The linear regression Eq. (9) demonstrates the relationship between the BOD removal percentages with an R² value of 0.8374 and with the residuals displaying a constant variance. However, in contrast, for COD, the F₀ values of all parameters were lower than the critical F₀ value, suggesting that under the investigated conditions none of the three factors or their interactions had any significant effect on COD removal.

$$\text{Color removal (\%)} = 21.75 + 5.21x_A + 6.55x_B + 4.71x_Ax_B \quad (8)$$

$$\text{BOD removal (\%)} = 68.44 + 7.32x_A + 7.15x_B \quad (9)$$

Where x_A and x_B are the coded variables of A and B, respectively.

Fig. 3 demonstrates the relationship between the experimental data for color removal (a), and BOD removal (b), predicted by using the regression Eqs. (8) and (9), respectively. It can be seen that all the experimentally derived data fit very well with those obtained from model equations, with R² equal to 0.9396 and 0.9154 for color and BOD removal, respectively.

3. Univariate Method

From the factorial design study results, the removal efficiencies

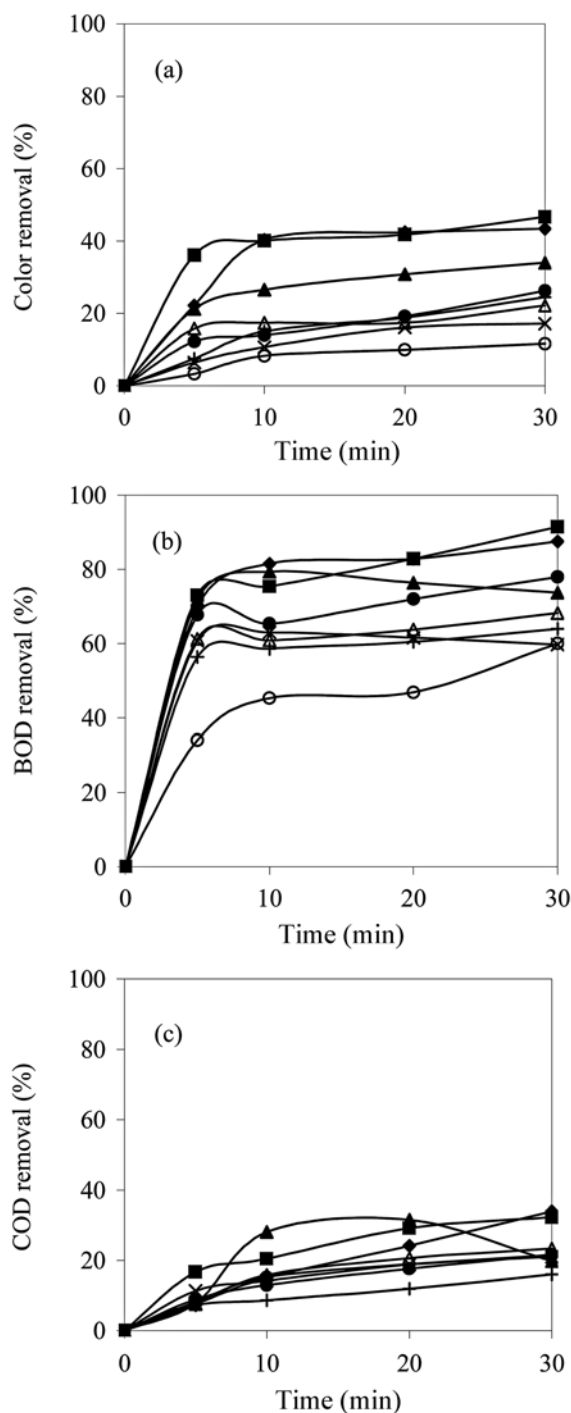


Fig. 2. Removal percentage of color (a); BOD (b); and COD (c) at various conditions. Conditions are outlined in Table 3 and are shown as I (+); II (×); III (●); IV (■); V (○); VI (▲); VII (△) and VIII (◆).

of color and BOD were affected only by the feed rates of H_2O_2 and Fe^{2+} whereas no parameter affected the COD removal efficiency. Furthermore, UV-A irradiation had no effect on color removal, which is contradictory to the published results of previous works [25,27], where although the removal of COD and color was correlated with the concentration of H_2O_2 and Fe^{2+} , respectively, consistent with this study, the UV irradiation in contrast was reported to favor color

removal in terms of rate per unit power [20]. Therefore, to verify the role of each main factor on pollutant removal, univariate analysis was adopted by changing the investigated ranges of all parameters one at a time. That is, the effect of the UV power was explored in the range of 60–120 W, the initial pH of wastewater within the range 5–9, the feed rate of Fe^{2+} within 3–9 ml/min and the feed rate of H_2O_2 in the range of 20–35 ml/min.

3-1. Effect of UV Power

The effect of UV light was explored at different UV powers ranging from 60–120 W under the controlled conditions of 5 ml Fe^{2+} /min, 25 ml H_2O_2 /min, initial pH of wastewater of 7 and a wastewater feed rate of 4 l/min. The wastewater had an initial level of color, BOD, COD and TDS of 3,230 Pt-Co unit, 424 mg/l, 3,360 mg/l and 1,542 mg/l, respectively. The results indicated that the UV-A power over 20 min affected the removal efficiency of color, BOD and COD in quite different ways (Fig. 4). Namely, the removal of color and COD increased slightly (40.6 to 57.2%) and significantly (13.3 to 47.6%), respectively, upon increasing the UV-A power from 60 W to 90 W, but further increases to the UV-A power above 90 W did not achieve any higher color or COD removal. However, the final percentage removal of color was still higher than that attained for COD, similar to the results of Kang et al. [20]. For BOD, close to 100% removal of BOD was attained by employing a UV-A power of 90 W for 20 min, as opposed to ~70% at 60 W, but further increasing the UV-A intensity above 90 W decreased the level of BOD removal attained. This may be due to the reduction of Fe^{3+} to Fe^{2+} according to reactions (3) and (4) at higher UV-A levels where the Fe^{2+} species can react with the dissolved oxygen leading to a decrease in the amount of dissolved oxygen in the treated wastewater as displayed by reaction (10) [28]. Therefore, a UV-A power of 90 W was deemed to be the optimum for treating textile wastewater by the photo-oxidation process in a continuous stirred tank reactor.



3-2. Effect of Initial pH of Wastewater

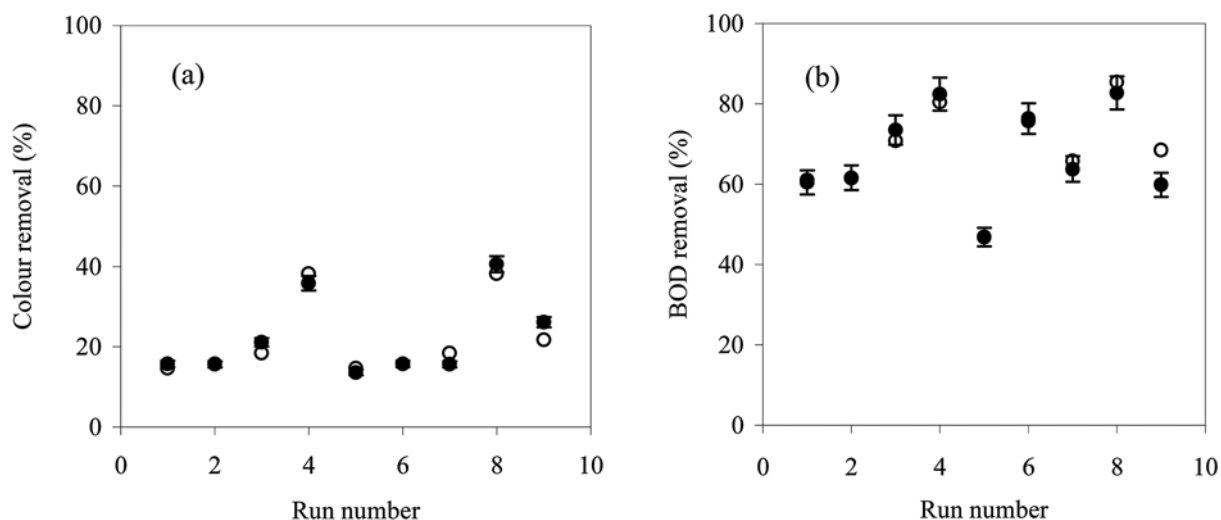
The optimum pH of the photo-Fenton reaction was reported to be around 3 by many researchers [29–32], because the main species produced at a pH of 2–3, $\text{Fe}(\text{OH})^{2+}(\text{H}_2\text{O})_5$, is the one with the largest light absorption coefficient and quantum yield for OH^\bullet production, along with Fe^{2+} regeneration, in the range 280–370 nm [29]. However, in actual textile plants, many cubic meters per day of textile dyeing wastewater are generated in the neutral pH range (Table 1). Adjusting the pH of such a large volume of wastewater to acidic pH, such as 2 or 3, is not practical for actual operation from both environmental and economic points of view. Therefore, the effect of varying the initial pH of wastewater in the range of pH 5 to 9 was assayed with a constant UV-A power of 90 W and feed rates of Fe^{2+} , H_2O_2 and wastewater of 5 ml/min, 25 ml/min and 4 l/min, respectively. The wastewater had an initial level of color, BOD, COD and TDS of 2,815 Pt-Co unit, 490 mg/l, 4,320 mg/l, and 1,560 mg/l, respectively. Increasing the initial pH of the wastewater from 5 to 9 decreased the removal efficiency for color, BOD and COD (Fig. 5). However, while BOD and COD showed no appreciable decline in removal between pH 5 and 7, but declined from pH 7 to 9 (~100 to 69.0% and 48.2 to 25.6%, respectively), color removal decreased slightly but significantly with increasing pH from 5 to 7 as well as 7 to 9 (67.3 to ~57 to 47.3%, respectively). These decreased removal

Table 3. Response of 2³ factorial designs at steady state condition designed by Design-Expert 6.0.10 version. A=feed rate of H₂O₂ (ml/min), B=feed rate of Fe²⁺ (ml/min) and C=intensity of UV-A (W)

Condition no.	Experiments	A	B	C	Color removal (%)		BOD removal (%)		COD removal (%)	
					Rep.1	Rep.2	Rep.1	Rep.2	Rep.1	Rep.2
I	(1)	-	-	-	11.5	14.5	64.8	63.1	14.4	17.5
II	a	+	-	-	22.3	17.2	59.7	59.8	20.6	21.3
III	b	-	+	-	32.1	26.3	71.6	65.7	22.9	20.3
IV	ab	+	+	-	37.5	46.7	92.9	90.0	33.3	31.3
V	c	-	-	+	18.5	11.7	53.3	66.7	20.8	22.1
VI	ac	+	-	+	18.7	34.0	78.6	85.3	20.0	19.5
VII	bc	-	+	+	15.9	22.2	70.0	66.4	25.0	21.7
VIII	abc	+	+	+	42.5	43.4	86.5	88.6	35.4	32.5
IX	Center	0	0	0	30.0	25.8	59.8	58.7	9.7	10.2

Table 4. ANOVA table

Source	Degree of freedom	Color removal			BOD removal			COD removal		
		Sum square	Mean square	F ₀	Sum square	Mean square	F ₀	Sum square	Mean square	F ₀
A	1	434.9	434.9	40.62	856.7	856.7	7.08	157.6	157.6	1.57
B	1	687.4	687.4	64.19	817.9	817.9	6.76	0.770	0.770	0.07
AB	1	355.4	355.4	33.19	1.920	1.920	0.016	34.52	34.52	0.34
C	1	1.912	1.912	0.178	17.18	17.18	0.14	78.94	78.94	0.79
AC	1	38.48	38.48	3.594	369.1	369.1	3.05	0.310	0.310	0.03
BC	1	0.386	0.386	0.036	27.88	27.88	0.23	132.37	132.37	1.32
ABC	1	15.83	15.83	1.479	84.36	84.36	0.70	60.68	60.68	0.60
Pure quadratic	1	46.49	46.49	4.342	69.55	69.55	0.570	41.53	41.53	0.41
Error	8	96.37	10.708		968.42	121.05		802.93	100.37	
Total	16	1667			3213			1309		

**Fig. 3. Comparison plots of the experimental data (●) and predicted values (○) for; (a) color removal using (13), and (b) BOD removal using (14).**

efficiencies with increasing initial pH are likely to be due to the coagulation of hydroxo-complex of Fe³⁺ formed during the reaction [33]. In addition, increasing the pH above neutral favors H₂O₂ decomposition decreasing the H₂O₂ levels and consequently the amount of OH[•] produced in the system [15,17]. According to the above re-

sults, the optimum initial pH of wastewater was deemed to be around 5, which is likely to be economically and environmentally feasible to attain in actual textile plants. At pH 5, under these conditions, approximately 61.0, 99.9 and 56.0% of color, BOD and COD were, respectively, removed and the final pH of the treated wastewater

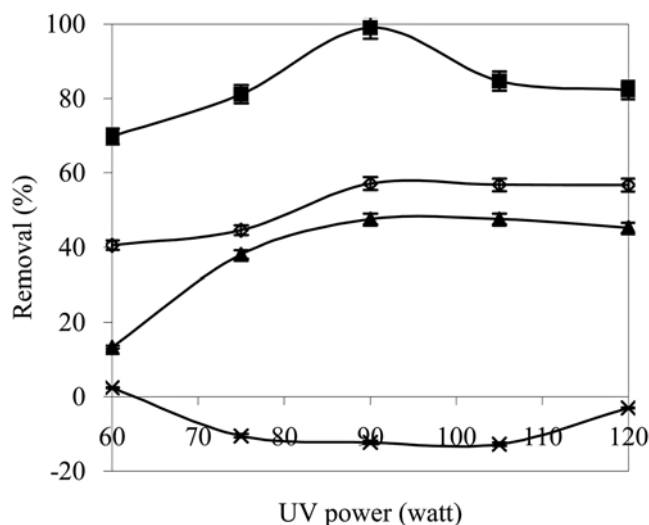


Fig. 4. Removal level (% of original) of pollutants as a function of UV-A power at 20 min operating time. Color (\diamond); BOD (\blacksquare); COD (\blacktriangle) and TDS (\times).

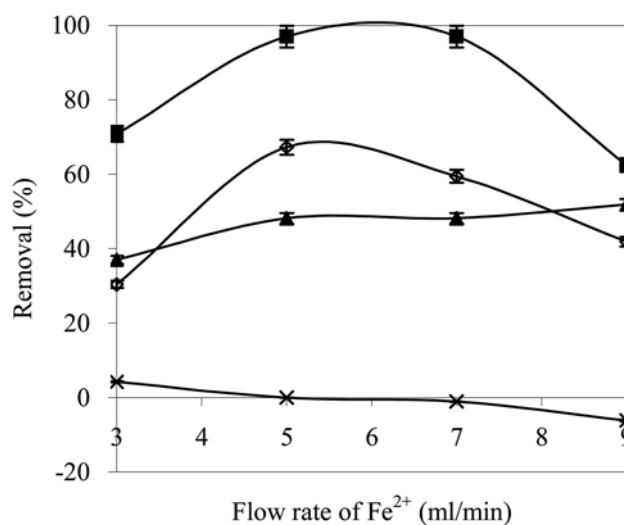


Fig. 6. Removal level (% of original) of pollutants as a function of feed rate of Fe^{2+} at 20 min operating time. Color (\diamond); BOD (\blacksquare); COD (\blacktriangle) and TDS (\times).

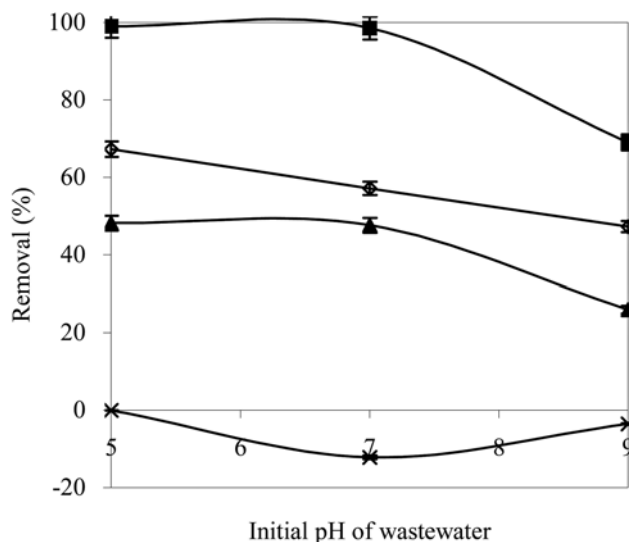


Fig. 5. Removal level (% of original) of pollutants as a function of initial pH at 20 min operating time. Color (\diamond); BOD (\blacksquare); COD (\blacktriangle) and TDS (\times).

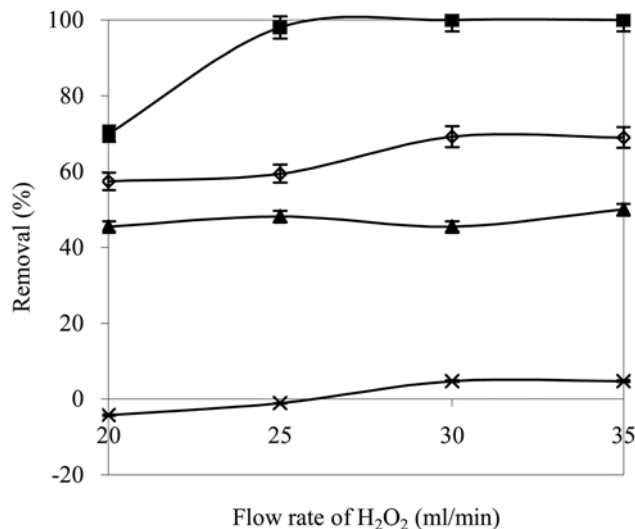


Fig. 7. Removal level (% of original) of pollutants as a function of feed rate of 30% (w/v) H_2O_2 at 20 min operating time. Color (\diamond); BOD (\blacksquare); COD (\blacktriangle) and TDS (\times).

was around 6.2, which are all within the permitted range for discharging directly into the environment.

3-3. Effect of Feed Rate of Fe^{2+}

The effect of Fe^{2+} dosage in the photo-oxidation process on the treatment of textile wastewater was investigated under different Fe^{2+} feed rates (3–9 ml/min) by using an initial pH of 5, UV-A power of 90 W, feed rate of H_2O_2 of 25 ml/min and feed rate of wastewater of 4 l/min. The wastewater had an initial level of color, BOD, COD and TDS of 1,001 Pt-Co unit, 490 mg/l, 4,320 mg/l and 2,292 mg/l, respectively. The results, summarized in Fig. 6, suggest that increasing the Fe^{2+} feed rate from 3 to 5 ml/min increased color, BOD and COD removal from 30.4 to 67.3%, from 70.8 to nearly 100%, and from 37.0 to 48.2%, respectively, due presumably to more OH^\bullet radicals being produced with the increased amount of Fe^{2+} in the sys-

tem to catalyze H_2O_2 to form OH^\bullet [34]. However, further increases in the Fe^{2+} feed rate led to a markedly decreased removal efficiency of color and BOD. In the case of color removal, this may be due to the regeneration of color contributed by the ferrous ions species [20], and additionally for BOD due to excess Fe^{2+} reacting with the dissolved oxygen in wastewater according to reaction (15). Given the increased removal of COD with Fe^{2+} feed rates of 7 and 9 ml/min were marginal compared to the significant decreases in BOD and color removal, a Fe^{2+} feed rate of 5 ml/min appeared as the optimum, in agreement with the factorial analysis.

3-4. Effect of Feed Rate of H_2O_2

The initial concentration of H_2O_2 is known to play an important role in the photo-oxidation of wastewater, and so the effect of H_2O_2 dosage in the photo-oxidation process on the treatment of textile

wastewater was investigated under different H_2O_2 feed rates (20–35 ml/min) by using an initial wastewater pH of 5, UV-A power of 90 W and a feed rate of Fe^{2+} and wastewater of 5 ml/min and 4 l/min, respectively (Fig. 7). The wastewater used in this part had an initial level of color, BOD, COD and TDS of 1,732 Pt-Co unit, 450 mg/l, 3,520 mg/l and 1,809 mg/l, respectively. Increasing the H_2O_2 feed rate from 20 to 25 ml/min dramatically enhanced the removal of BOD (70 to ~99%) with no further improvement with increasing H_2O_2 levels. Although color removal was also improved by increased H_2O_2 feed rates, this was less marked and occurred upon increasing the feed rate from 25 to 30 ml/min (57.0 to ~69%) with no further improvement at higher H_2O_2 feed rates due to scavenging of OH^\bullet radicals at high H_2O_2 concentrations (Reactions (11) to (13)) [22,35]. In contrast, the slight increase in COD removal (45.5 to ~50%) required the highest tested feed rate (35 ml/min), but is compounded by the fact that excess H_2O_2 interferes with the measurement of COD [18]. Therefore, an optimal feed rate is likely to be around 30 ml H_2O_2 /min but, given that H_2O_2 is expensive (approximately 22.25 USD/liter, Ajax), a feed rate of 25 ml/min of H_2O_2 can be used as the optimum economic feed rate for the continuous treatment system.



In all these cases, the TDS content of the wastewater considerably increased upon treatment with all conditions of the photo-oxidation process (Figs. 4–7). This can be explained by the formation of new species or the intermediate oxidation products and, in the presence of UV-A light, the formation of by-products as a result of dye photolysis and higher degree of mineralization [13].

Table 5 displays a comparison of pollutant removal obtained from this work compared to other published works. Note that all previous works were performed in a batch reactor. The adsorption process provided a high removal efficiency of color but only poor BOD removal, whereas this work in a continuous flow had a high removal percentage of BOD but only medium level color removal. The coagulation process provided a little bit lower removal percentage of color, and a little bit higher removal percentage of COD than those of this work. However, the former worked with a synthetic solu-

tion that contained a low concentration of pollutants, whereas this study used real textile wastewater with higher initial pollutant levels. The treatment of textile wastewater by a photo-Fenton oxidation process in batch reactor [25] attained a higher color and slightly higher COD removal efficiency compared with this work, although there is no corresponding data on BOD removal for comparison. However, this work was done in a continuous process with no recycle stream. Thus future work, to improve the performance of this continuous process, should evaluate the use of a recycle stream and some parameters should be further adjusted in a factorial design to attain a higher removal efficiency. The properties of the treated textile wastewaters (Table 1) revealed that the pH, and level of TDS, color and BOD were all within the current acceptable values for discharge into the environment set by the Thai government except COD levels, which were still higher than acceptable discharge values by approximately 4-fold. The remaining COD in the treated wastewater could easily be economically and practically further reduced by settling in aeration ponds.

CONCLUSIONS

To have both industrial and environmental relevance, the ability to remove color, BOD and COD from textile wastewater by the photo-oxidation process with $\text{UV}/\text{H}_2\text{O}_2/\text{Fe}^{2+}$ reagents was investigated using real and not synthetic textile wastewater and a continuous stirred tank reactor, by using a 2^4 factorial design together with the univariate methods. The photo-oxidation process reached a steady state condition in the continuous reactor within 5–10 min and the H_2O_2 and Fe^{2+} feed rates and UV-A power were found to affect the color and BOD removal, whereas only UV-A intensity affected COD. The optimum condition was found at a UV-A power of 90 W, initial wastewater pH of 5, feed rate of Fe^{2+} of 5 ml/min, and feed rate of H_2O_2 of 25 (economic) or 30 (actual) ml/min. Under such conditions, approximately 69.2, 99.4 and 48.5% of color, BOD and COD, respectively, were reduced. However, during the treatment process, the concentration of TDS increased, presumably due to the formation of new species or the intermediate oxidation products. Nevertheless, all values of pollutants in the treated wastewater except COD were lower than the Thai government standard values and below the maximum levels permitted for direct discharge into the environment. Our optimal condition is still effective if the level of pollut-

Table 5. Comparison of removal efficiency of all pollutants in this work with other published works

Author (Year)	Type of treatment process	Type of wastewater	Color		COD (mg/l)		BOD (mg/l)	
			Level	%	Level	%	Level	%
This work	Photo-Fenton oxidation (Continuous)	Wastewater from textile plant	1,001–3,230 Pt-Co unit	69.2	3,360–4,320	48.5	424–490	99.4
Sahunin et al. [25]	Photo-Fenton oxidation (Batch)	Wastewater from textile plant	1,584–2,310 Pt-Co unit	90	2,500–27,000	52	-	-
Marco and Jose [27]	Photo-Fenton oxidation (Batch)	Synthetic wastewater (RB 5)	1.0×10^{-4} M	98.1	-	-	-	-
Kadirvelu et al. [36]	Adsorption by activated carbon (Batch)	Dyeing wastewater	-	100	196–844	56	18–152	35
Selcuk [37]	Sulfate coagulation (Batch)	Synthetic cotton textile mill	$1.02\text{--}1.37 \text{ m}^{-1}$	50–60	1,150	60	-	-

ant in wastewater is lower than the maximum values displayed in Table 5. In case of too high level of pollutants in wastewater, the efficiency of the treatment system will be reduced; the new optimization condition should be explored.

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