

Optimization of the Photochemical Degradation of Textile Dye Industrial Wastewaters

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In this study, the photochemical degradation via photo-Fenton process was carried out to degrade dyes in textile industrial wastewaters. Experimental design methodology was also applied for optimizing effects of factors which influence the effective treatment such as ferric dose, hydroperoxide dosage, initial pH, reaction time and initial chemical oxygen demand (COD). Two independent variables namely colour and COD removal efficiencies were used to evaluate the treatment yield. Under the optimal conditions, ca. 99% and ca. 88%, colour, and COD were removed, respectively.

Key words: Photo-Fenton; textile industrial wastewater; design of experiment

Recently, Vietnam's textile and garment industry are playing a significant role in national socio-economic development (Agency VTP 2014). However, this sector consumes a lot of water (EPA 1996). Consequently, it is also one of largest groups of industries causing severe water pollution (Torrades & García-Montaña 2014); they also mentioned that textile mills damaged the quality of the environment by emitting high suspended solids, high temperature, unstable pH, high chemical oxygen demand (COD), low biological oxygen demand (BOD) as well as great colourization (Torrades & García-Montaña 2014).

On the other hand, textile wastewater usually contains organic compounds which are unable to be degraded by biological or even chemical treatments (Uygur & Kök 1997; dos Santos *et al.* 2007) and can be harmful to environments (dos Santos *et al.* 2007).

Up to now, various methods at the laboratory, pilot or full-scale have been applied for textile wastewater treatment. However, most of them are quite inefficient due to toxic and non-biodegradable substances of textile wastewaters (dos Santos *et al.* 2007; Forgac *et al.* 2004). To overcome some drawbacks of currently mentioned methods, researchers focus on advanced oxidation processes (AOPs) such a photo-catalysis method. Typically, Fenton and photo-Fenton techniques which were reported in few published articles have been carried out for treating textile wastewaters (Alinsafi *et al.* 2007; Lucas & Peres 2006; Meric *et al.* 2004; Lee & Shoda 2008) especially the removal of COD and colourization (Uygur & Kok 1999; Forgaes *et al.* 2004; Meric *et al.* 2004; Lee & Shoda 2008; Arslan-Alaton *et al.* 2009) because of their advantages (Torrades & Garcia-Montana 2014; Arslan-Alaton *et al.* 2009). Moreover, José Blanco *et al.* (2012) carried out experiment on textile wastewater via the combination

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of Fenton and biological-Fenton coupled processes. They concluded that Fenton reaction and combination of biological treatment and Fenton reaction were proper treatments to this kind of wastewater. According to the results, Fenton process should be followed by biological treatment for saving energy and cost.

In the experimental point of view, the design of the experiment (DOE) was also employed to find out the optimal conditions of independent variables to overcome some disadvantages of the one-factor-at-a-time method such as more runs, without interaction information or missing optimal setting of factors (Hartmann *et al.* 2010; Montgomery 2005; Tan-Hiep & Chen 2013). Therefore, this study presents the application of 2-level fractional factorial design for degrading textile dye wastewater via the photo-Fenton process.

MATERIALS AND METHODS

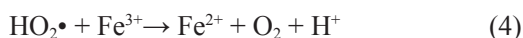
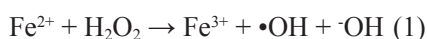
Samples and Chemicals

Characteristics of six loads of textile wastewater (TW) samples gathered from the textile and garment industrial zones in Ho Chi Minh City, and Khanh Hoa Province (Vietnam) were mentioned in *Table 1*.

COD and colour of all collected samples were analyzed according to fulfill using APHA standards (Standard Methods) (APHA 1998). Other chemicals were also of standard analytical reagents. The taken samples were stored at 4°C before use.

Fenton and Photo-Fenton's Reaction

Fenton's reaction is the dark reaction of ferrous iron (Fe^{2+}) with H_2O_2 . It is a series of reaction to generate $\bullet\text{OH}$ radicals and Fe^{2+} ion.

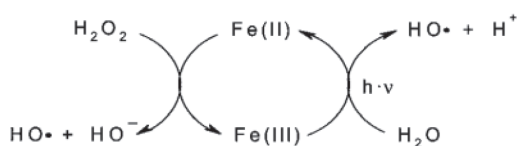


More recently, some researchers integrate the UV radiation and ozone with Fenton's reaction for treating the toxic wastes (Forgaes *et al.* 2004; Arslan *et al.* 2009; Hartmann *et al.* 2010). The mechanism of the Fenton and photo-Fenton's reaction *Scheme 1* was reported in the published literature (Arslan-Alaton *et al.* 2009; Sohrabi *et al.* 2014).

Table 1. Values of colour and chemical oxygen demand of taken textile wastewaters.

Loads	Colour, PCU ^(a)	COD (ppm)
A ^(b)	761.3	249 .0
B ^(b)	774.7	161 .0
C ^(c)	19 760–31 616	428.8–686.1
D ^(c)	23 712–35 568	514.6–772.0
E ^(c)	33 592–41 496	729.0–900.5
F ^(c)	31 616–39 520	686.1–857.6

^(a) Platinum-cobalt Unit; ^{(b), (c)} Stand for samples taken from industrial zones in Khanh Hoa Province, and Ho Chi Minh City, respectively.



Scheme 1. Mechanism of the photo-Fenton's reaction (Arslan-Alaton *et al.* 2009).

Kusic H. *et al.* (2006) mentioned that the Fenton's techniques and a combination of UV and H_2O_2 are the widely used methods compared to other chemical AOPs. Therefore, photo-Fenton in which ferric ion instead of ferrous ion was applied in this case.

Experiments

In this work, the photo-Fenton's reaction took place in a glass-jacket immersion-type UV-reactor which was modified from the system developed by Hansson *et al.* (2012).

All runs were carried out with a volume of 0.5 l of textile wastewaters. All investigated parameters were listed in Table 2, while the unlisted ones such as agitation speed and temperature reaction were kept constant as 400 rpm and ca. 30°C, respectively. In this case,

water was used as a coolant to maintain the reaction temperature constant.

After the desired durations, the pH value of the treated wastewaters was neutralized to ca. 6.5 and continuously agitated for 5 min at 400 rpm for quenching the photo-Fenton reaction, while the UV radiation was switched off (Zhu *et al.* 2011).

Design of Experiment and Statistic Analysis

According to the published literatures (Uygun & Kok 1999; Alinsafi *et al.* 2007; Lucas & Peres 2006; Meric *et al.* 2004; Lee & Shoda 2008; Arslan-Alaton *et al.* 2009; Hartmann *et al.* 2010; Sohrabi *et al.* 2014; Kusic *et al.* 2006), the main factors or independent variables that can influence the removal efficacy of COD and colour from textile wastewater are initial pH, UV radiation duration (min), dosage (mmol) of Fe(III) and H_2O_2 (HP) as well as the original COD (ppm), while the response variables are removal efficiency of colour (Y1, %) and COD (Y2, %).

In this report, the fifth batch was selected as a demonstration of the application of design of experiment to do research in environmental issues. Uncoded and coded factors with their

Table 2. The uncoded/coded factors and their concerned levels in this work.

Uncoded/ Coded	Name of factors	Factor levels	
		Low (-1)	High (+1)
pH/ X_1	pH	3.0	4.0
t/X_2	UV radiation duration (min)	30	40
Fe(III)/ X_3	Dosage of Fe(III) (mmol)	0.75	1.0
HP/ X_4	Dosage of H_2O_2 (mmol)	8.0	12.0
COD/ X_5	Initial COD (ppm)	729.0	900.5

levels were listed in *Table 2*.

All statistical analyses, and design of experiment were done by using *MS-Excel* with calculated appropriate formula were conducted by Montgomery 2005 (Tân-Hiệp & Chen 2013) as well as with a statistical software viz. SAS JMP®. The response variables were predicted by using the first-order equation as below in *Equation 5*.

$$\hat{Y} = \beta_0 + \sum_{j=1}^k \beta_j X_j + \sum_{i < j} \beta_{ij} X_i X_j + \varepsilon \quad (5)$$

where k , \hat{Y} , β_j , β_{ij} and ε mean number of independent variables, predicted the response variable, linear regression coefficients, interactive coefficients, and the residual or random error, respectively (Montgomery 2005).

In this study, a two-level fractional factorial design (FFD) for fitting the first-order model expressed as *Equation 5*, shown in *Table 3* was duly carried out. The patterns, the dependent (Y) and predicted (\hat{Y}) dependent variables were listed in *Table 3*, respectively.

The last row in *Table 3* describes the average results gained from the experiments conducted at the central point. Also, the run order was randomly performed to minimize errors.

Table 3. The patterns, response and predicted response variables.

Patterns	Y ₁ (%)	Y ₂ (%)	\hat{Y}_1 (%)	\hat{Y}_2 (%)
---- +	75.6	46.7	75.6	44.9
+----	61.8	35.9	61.8	36.6
-+---	86.6	55.2	86.6	55.5
++--+	75.0	51.7	75.0	52.5
-+--	86.1	59.6	86.1	61.4
+--++	78.6	55.2	78.6	54.5
-++-+	77.7	53.1	77.7	52.8
+++--	87.4	60.5	87.4	59.7
---+-	97.3	64.9	97.3	64.1
+--++	68.7	41.0	68.7	40.7
-+--+	90.7	60.9	90.7	60.2
++-+-	94.7	58.7	94.7	60.5
--+++	92.3	62.3	92.3	63.1
+---+	65.6	29.8	65.6	30.1
-+++-	97.0	69.3	97.0	70.0
+++++	92.4	70.9	92.4	69.1
00000	89.9	58.9	–	–

RESULTS

Examination of Untreated Textile Wastewater

The taken TWs were characterized by monitoring parameters such as initial pH, COD, colour, and surfactants, and *Table 1* shows the extracted results.

Statistical and Multiple Regression Analysis

Effects of main factors and interactions.

Figure 1 shows the influence of five main factors on the removal efficacy of colour and COD in the case of the fifth batch of TW.

Two first and the fourth variables (X_1 , X_2 and X_4) would be strongly affected by removal efficiency, while the third and the last one would be of insignificant influence. Therefore, the higher levels of X_2 and X_4 the higher

efficiencies of both colour and COD removal could be obtained because of their positive linear influence. The influences of X_1 and X_2 on the dependent variables are quite similar but in an opposite direction. Typically, the initial pH value should be decreased to get higher colour and COD removal. Those are also the strongest effects. This statement is consistent with the conclusion of low pH values as running the Fenton's or photo-Fenton reaction (Arslan-Alaton *et al.* 2009; Hansson *et al.* 2012).

In the interaction point of view, the highest effect resulted from the interaction between initial pH and UV radiation duration (X_1X_2) in both colour and COD removal. The effects of the rest are moderate and presented in *Table 4*. In this case, the higher interactions were neglected because of their insignificant effects. *Table 4* expresses an ANOVA analysis for the reduced models at probability of 95.0%.

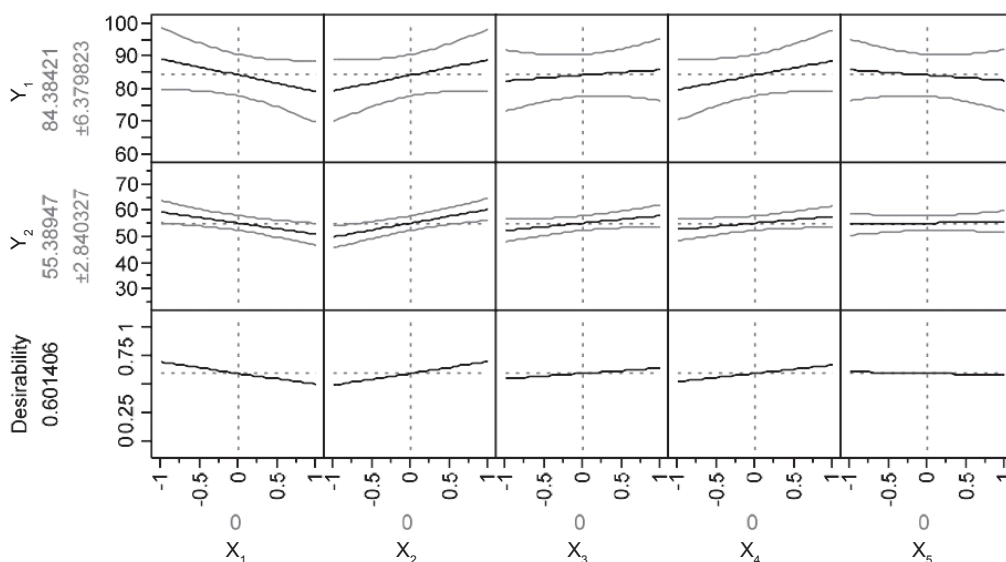


Figure 1. Effects of main factors on response variables.

Table 4. ANOVA for reduced models.

Terms	t ^(d)	t ^(e)	Terms	t ^(d)	t ^(e)
Inter.	466.4	252.8	X_1X_4	11.5	13.2
X_1	27.8	19.7	X_2X_3	–	–
X_2	26.5	24.5	X_2X_4	9.2	11.2
X_3	9.4	13.2	X_3X_4	12.3	9.3
X_4	24.6	11.5	$X_1X_2X_3$	–	4.9
X_5	9.0	–	$X_1X_2X_4$	12.4	10.6
X_1X_2	26.0	21.6	$X_1X_3X_4$	12.1	6.4
X_1X_3	7.3	–	$X_2X_3X_4$	12.6	17.3

^{(d),(e)} Stand for Y_1 and Y_2 , respectively.

The reduced models for colour (\hat{Y}_1) and COD (\hat{Y}_2) are expressed in *Equations 2–3*, respectively.

$$\hat{Y}_1 = 82.97 - 4.94X_1 + 4.72X_2 + 1.67X_3 + 4.37X_4 - 1.59X_5 + 4.63X_1X_2 + 1.13X_1X_3 - 2.04X_1X_4 + 1.64X_2X_4 - 2.18X_3X_4 + 2.21X_1X_2X_4 - 2.14X_1X_3X_4 + 2.24X_2X_3X_4 \quad (6)$$

$$\hat{Y}_2 = 54.73 - 4.27X_1 + 5.31X_2 + 2.86X_3 + 2.49X_4 - 0.49X_5 + 4.68X_1X_2 - 2.86X_1X_4 + 2.42X_2X_4 - 2.01X_3X_4 + 1.06X_1X_2X_3 + 2.29X_1X_2X_4 - 1.38X_1X_3X_4 + 3.74X_2X_3X_4 \quad (7)$$

Checking model adequacy. The determine coefficient values, R^2 , of 99.49% for decolouration and 99.26% COD removal meant that not only a good agreement between predicted and observed values but also the obtained mathematical models, *Equations 6–7*, could predict the removal efficiencies very well (Montgomery 2005; Tân-Hiệp & Chen 2013).

Furthermore, F_{exp} values of these models were 9.7 and 8.3 respectively. In comparing to $F_{\alpha,df1,df2}$ of 19.0, these models were significant. Hence, they could be used for predicting the experimental results, *Figure 2*.

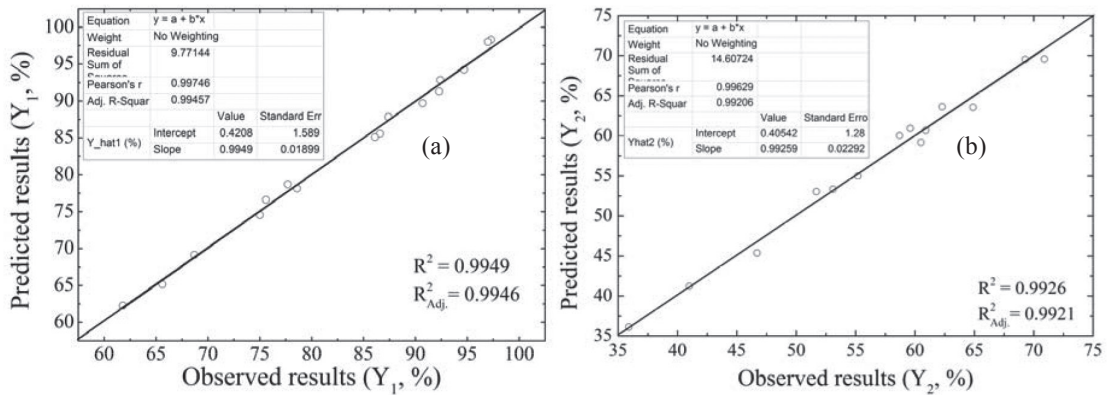


Figure 2. Observed vs. predicted removal efficiencies of colour (a) and COD (b).

Optimization. The analyses obtained above implied that the actual optimum was outside these operating conditions previously investigated. Thus, the steepest ascent method was preferentially called up to find out the optimal operation conditions. The as-fitted multi-linear models shown as *Equations 6–7*, were used in this paper. The path of the steepest ascent is the line through the center of FFD moving the fastest to the fitted surface. Usually, it will go until no further increment in response is observed (Montgomery 2005; Tan-Hiep & Chen 2013).

In this study, the optimal condition is 2.70 of initial pH, the duration time of ca. 51 min, and 0.975 and 12.00 mmol of ferric and HP dose, respectively. Under the optimum condition, efficacies of colour and COD removal could be attained as high as of ca. 99.5% for decolouration and ca. 88.0% for COD removal.

CONCLUSIONS

Photo-Fenton's reaction using ferric could be conducted for degrading dyes in textile and garment wastewater collected from an industrial park in Khanh Hoa as well as Ho Chi Minh City (Vietnam).

It could be successful to apply DOE especially FFD for solving not only the specific example in this study (colour and COD removal) but also other problems of environmental engineering.

These optimal conditions were summarized as: (1) initial pH value of 2.7; and (2) UV radiation duration of ca. 51 min, the dosage of ferric and HP respectively of 0.975 and 12.00 mmol, and stirring speed of 400 rpm. The positive point of this study was the quality of treated TW which satisfied the Vietnam National Standards (Type B).

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