



Chapter 4

Results and Discussions

4.1 Carriers characterization

Fluidized-bed Fenton process lets ferric ion (Fe^{3+}), produced in the Fenton reaction, be transformed into iron oxide (FeOOH) onto the carrier surface via the crystallization or sedimentation. This process combines the functions of homogeneous chemical oxidation ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$), heterogeneous chemical oxidation ($\text{H}_2\text{O}_2/\text{FeOOH}$), fluidized-bed crystallization, and reductive dissolution of FeOOH . Heterogeneous Fenton processes are of particular interest, since most of the iron remains in the solid phase. The solid phase is usually granular (metal oxides or sand), hence the treated water is easily separated from the iron.

In this study, aluminum oxide (Al_2O_3) and silica oxide (SiO_2) were used to compare the efficiency of color and COD removal. Aluminum oxide average particle diameter is 2.5 mm and the particle diameter of silica oxide is between 0.84 and 2.00 mm.

The investigated pH_{pzc} value in pure water of Al_2O_3 and SiO_2 are 8.21 and 5.80, respectively. These results mention that the positive surface charge is pH lower than pH_{pzc} of media and the negative surface charge is pH higher than pH_{pzc} of media. As the investigated experimental study in fluidized-bed Fenton process was deal with acidic pH. Therefore, pH_{pzc} value of these media was performed as the positive surface charge (Table 4.1).

Table 4.1 Diameter, surface area, pore size and pH_{pzc} of different carriers.

Carriers	Average Diameter (mm)	Surface area (m^2/g)	Pore size (A°)	pH_{pzc}
Al_2O_3	2.50	314	10.89	8.21
SiO_2	1.42	0.001462	0	5.80

4.2 Control experiment (adsorption)

The results show that part of target compounds was decomposed without Fenton's reagent. Figure 4.1 shows the color and COD remaining obtained all control experiments versus time. The portion of color and COD being removed in 100 minutes by adsorption in the absence of H_2O_2 and Fe^{2+} were shown in the Table 4.2.

Table 4.2 Color and COD removal efficiency of reactive dyes in control experiments (adsorption) (Appendix A).

Carriers	% Color removal			% COD removal		
	RB 5	RO 16	RB 2	RB 5	RO 16	RB 2
Al ₂ O ₃	88.84	15.61	83.43	67.57	1.59	56.25
SiO ₂	0.46	0.85	1.33	6.94	5.26	5.80

Table 4.2 and Figure 4.1 exhibited that in control experiments, the color and COD removal efficiencies of reactive dyes of carriers as Al₂O₃ system were much higher than SiO₂ system due to adsorption onto the surface of carriers, except COD removal efficiency of reactive orange16 of carriers as Al₂O₃ system was lower than SiO₂ system due to after the reaction started 5 minutes, the COD onto the surface of Al₂O₃ against dissolved in the water.

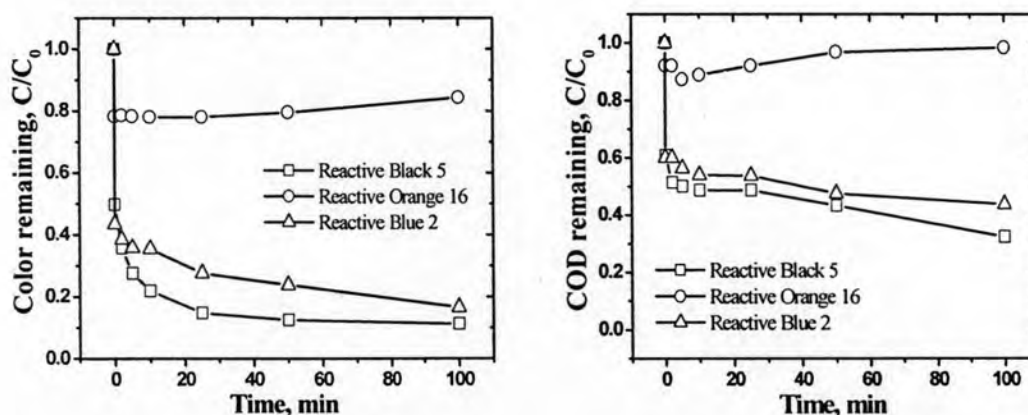


Figure 4.1a Control experiments in fluidized-bed reactor; reactive dyes = 0.1 mM, Al₂O₃ = 74.07 g/l and initial pH = 3.0.

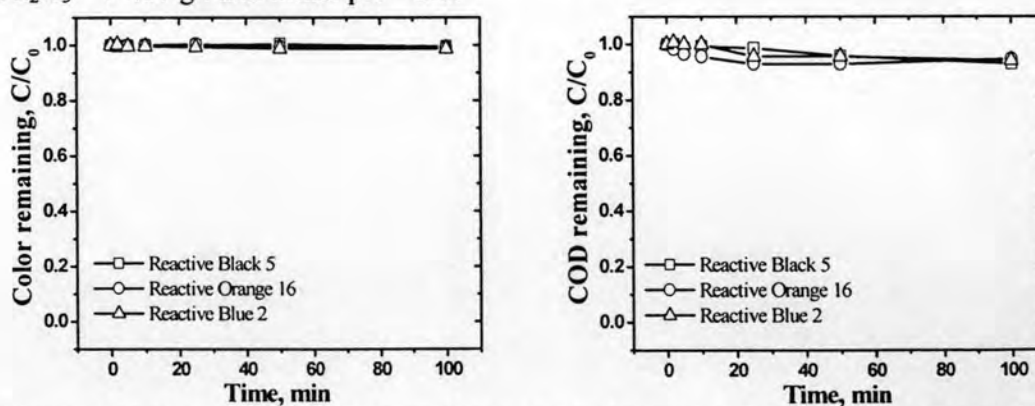


Figure 4.1b Control experiments in fluidized-bed reactor; reactive dyes = 0.1 mM, SiO₂ = 74.07 g/l and initial pH = 3.0.

Figure 4.1 Comparison of different carriers, control experiments in fluidized-bed reactor (adsorption).

4.3 Comparison of different carriers

The comparison of different carriers, aluminum oxide (Al_2O_3) and silica oxide (SiO_2) were investigated onto the color and COD degradation of synthetic reactive dyes; reactive black 5, reactive orange 16 and reactive blue 2. As Fenton's reagent produce hydroxyl radical can lead to oxidize the organic compound, fluidized-bed Fenton can reduce the amount of iron oxide which is the drawback of Fenton process. In previous study (Khunikakorn, 2006), aluminum oxide and silica oxide were used to be the carriers in fluidized-bed Fenton process effectively. In this study, the carriers which have different basic elements were operated in this scenario in order to determine the carrier was used for all experiments.

The carriers which have different basic elements were operated in this scenario. Because the pzc of Al_2O_3 and SiO_2 were 8.21 and 5.80 as mentioned from previous study. Each carrier was used 74.07 g/l. The Fenton system for color and COD degradations was suitable adjusted for the initial acidic pH, 3.0 for all experiments (Hsueh et al., 2005).

Figure 4.2 exhibited the comparison of different carriers on the reactive dyes degradation which the target compounds; reactive black 5 (RB5), reactive orange 16 (RO16) and reactive blue 2 (RB2). The color removal efficiencies of RB5 and RB2 of the carriers as SiO_2 system are higher than Al_2O_3 system and the color removal efficiencies of RO16 of the carriers as Al_2O_3 system are closed. The SiO_2 system, the color removal efficiencies of RB5, RO16 and RB2 were 98.7%, 98.9% and 98.0%, respectively. The Al_2O_3 system, the color removal efficiencies were 98.3%, 99.9% and 82.3%, respectively. Together with COD removals the SiO_2 system; 91.2% RB5, 66.3% RO16 and 79.0% RB2 were higher than Al_2O_3 system; 65.8% RB5, 56.8% RO16 and 60.6% RB2 that were shown in Table 4.3.

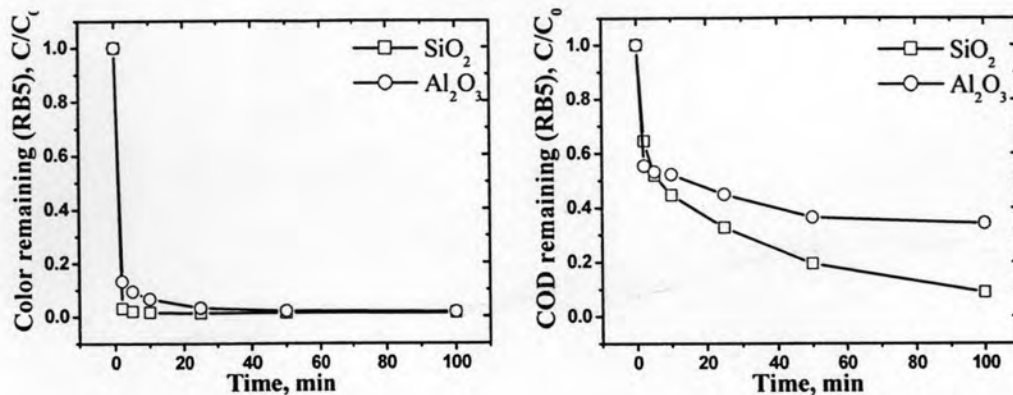


Figure 4.2a Comparison of different carriers on the reactive black 5 degradation; RB5 = 0.1 mM, Fe^{2+} = 20 mg/l, H_2O_2 = 160 mg/l, carrier = 74.07 g/l, initial pH = 3.

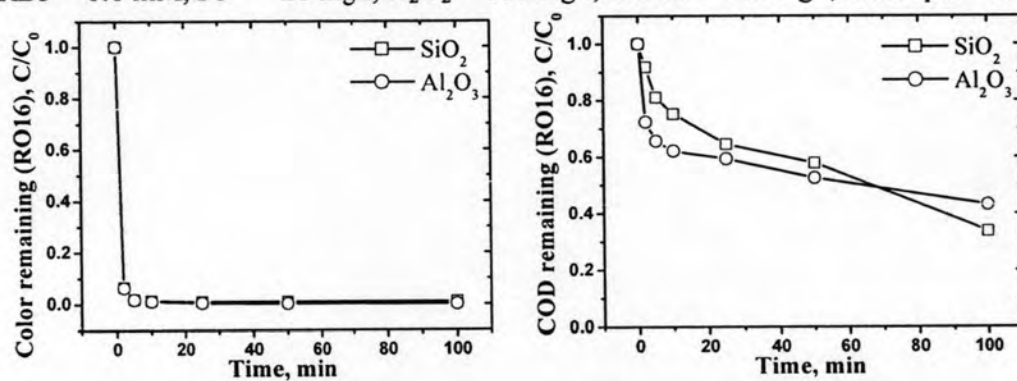


Figure 4.2b Comparison of different carriers on the reactive orange 16 degradation; RO16 = 0.1 mM, Fe^{2+} = 10 mg/l, H_2O_2 = 160 mg/l, carrier = 74.07 g/l, initial pH = 3.

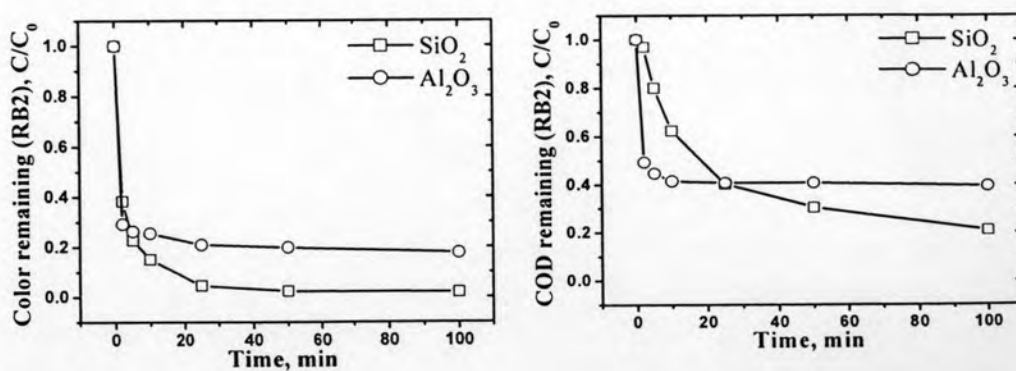


Figure 4.2c Comparison of different carriers on the reactive blue 2 degradation; RB2 = 0.1 mM, Fe^{2+} = 15 mg/l, H_2O_2 = 160 mg/l, carrier = 74.07 g/l, initial pH = 3.

Figure 4.2 Comparison of different carriers on the reactive dyes degradation.

Table 4.3 Comparison the color and COD removal efficiency of different carriers on the reactive dyes degradation (Appendix B).

Reactive Dyes	% Color removal		% COD removal	
	SiO ₂	Al ₂ O ₃	SiO ₂	Al ₂ O ₃
RB5	98.7	98.3	91.2	65.8
RO16	98.9	99.9	66.3	56.8
RB2	98.0	82.3	79.0	60.6

From the results of the control experiment (adsorption) in Table 4.2, color and COD can be removed by adsorption. Color and COD in the wastewater moved to attach onto the surface of carriers. After adding Fenton's reagent in the Al₂O₃ systems, Fenton's reagent reacted with color and COD on the surface of carriers much more than those in the wastewater. Color on the surface of Al₂O₃ carriers in control experiments (adsorption) was stronger than that in fluidized-bed Fenton systems which were shown in Figure 4.3.

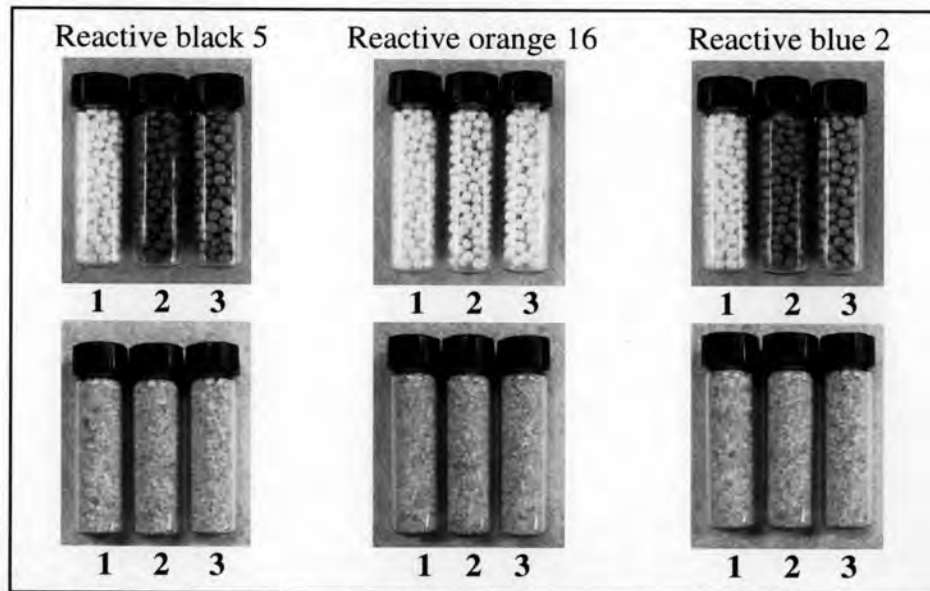


Figure 4.3 Carriers in control experiments (adsorption) and fluidized-bed Fenton systems; Al₂O₃ (Top), SiO₂ (Bottom).

***REMARK: 1.Original carrier 2.Adsorption 3.Fluidized-bed Fenton process

Color and COD removal efficiency of reactive dyes in Al₂O₃ system were lower than those in SiO₂ system. This research was investigated the oxidation rate of color and COD removal not adsorption, therefore, the chosen carrier was SiO₂. For the next scenario, the SiO₂ were conducted go through all of experiment as the carrier in the system of fluidized-bed Fenton process.

4.4 Color and COD removals of synthetic dyeing wastewater

In this study, color and COD removals are used as the indexes to evaluate the performance of fluidized-bed Fenton process. For the purpose of color removal, 1-5 mg/l of ferrous ions were enough but for COD removal, higher ferrous dosage was needed. Therefore, two categories of experimental conditions were designed for color and COD removals. However, both color and COD values of all samples were measured for comparison.

4.4.1 COD removals of synthetic dyeing wastewater

4.4.1.1 Effect of Fe^{2+} on the COD removal efficiency of reactive dyes

The effect of Fe^{2+} concentration on color and COD removal efficiencies for 0.1 mM of reactive dyes under the conditions of $\text{H}_2\text{O}_2 = 160$ mg/l, $\text{SiO}_2 = 74.07$ g/l, $\text{pH} = 3.0$, and $\text{Fe}^{2+} = 5 - 25$ mg/l, is given in Figure 4.4. From Figure 4.4, it is clear that COD removal increased with increasing Fe^{2+} concentration. At 100 minutes, the COD removals of reactive dyes are shown in Table 4.4. At the same time, more than 96% of color removal was obtained at all Fe^{2+} concentrations (5-25 mg/l). This increasing trend is due to that the higher the ferrous dosage, the more the $\text{OH}\cdot$ can be formed through Fenton reaction, thus leading to a higher rate of color and COD removal.

Under different ferrous dosages, the statistical data of pseudo-second order rate constants of COD removal, which are listed in Table 4.4 and Figure 4.5, serve to demonstrate quantitatively their enhancing effect on the COD removal. Note that the statistical data calculation was based on the assumption of pseudo-second order reaction kinetics within the reaction period from 0 to 100 min as shown below:

$$(1/[A]) = (1/[A]_0) + kt$$

where $[A]$ is the COD value at reaction time, t , $[A]_0$ is the initial COD and k is the rate constant.

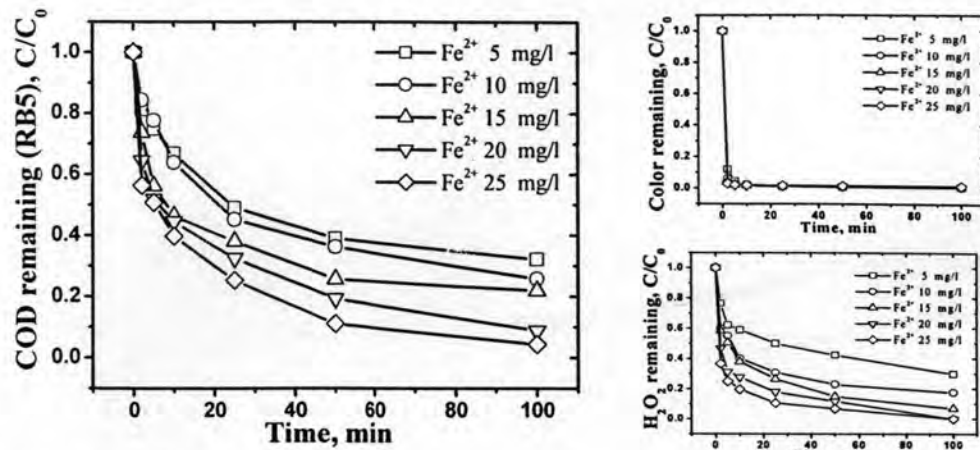


Figure 4.4a Effect of Fe^{2+} concentration on COD removal of RB5; RB5 = 0.1 mM, H_2O_2 = 160 mg/l, carrier = 74.07 g/l, initial pH = 3.

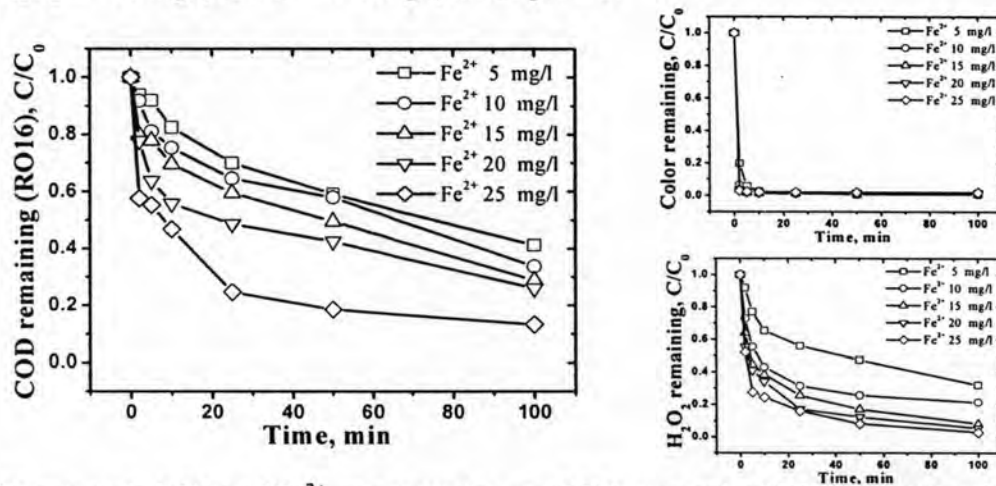


Figure 4.4b Effect of Fe^{2+} concentration on COD removal of RO16; RO16 = 0.1 mM, H_2O_2 = 160 mg/l, carrier = 74.07 g/l, initial pH = 3.

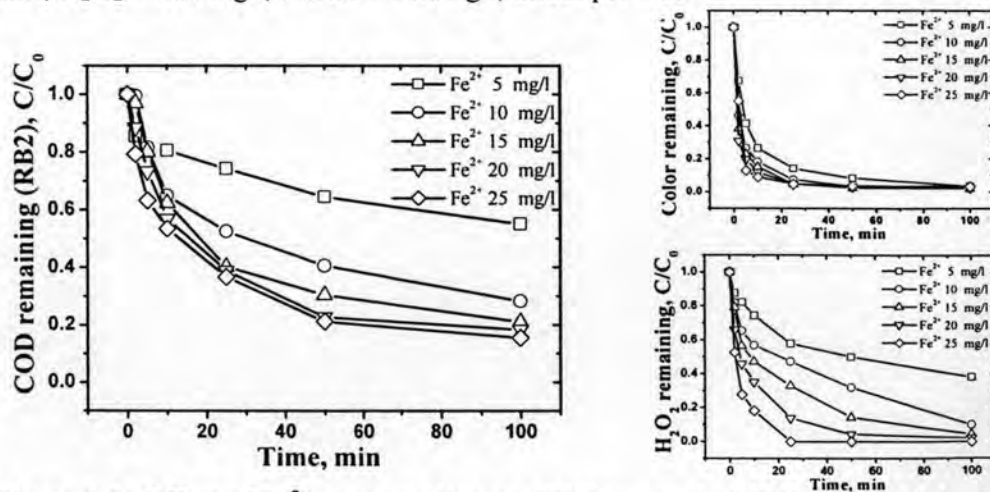


Figure 4.4c Effect of Fe^{2+} concentration on COD removal of RB2; RB2 = 0.1 mM, H_2O_2 = 160 mg/l, carrier = 74.07 g/l, initial pH = 3.

Figure 4.4 Effect of Fe^{2+} concentration on COD removal of reactive dyes.

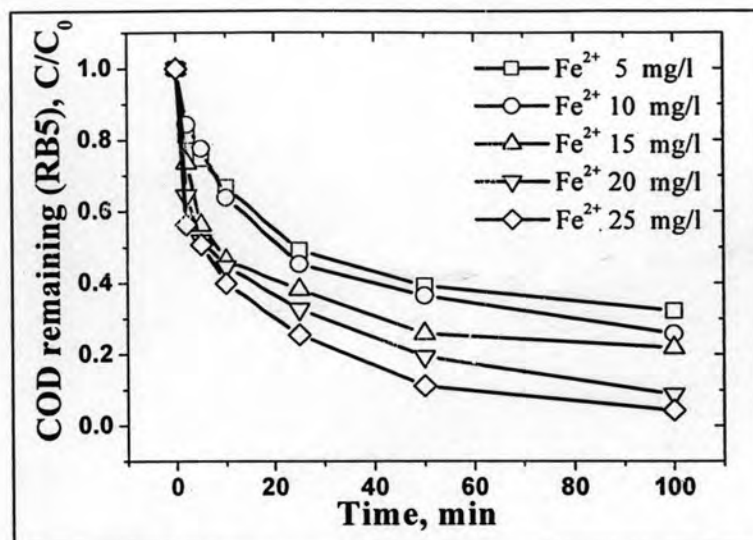


Figure 4.5a Effect of Fe^{2+} concentration on COD removal of RB5.

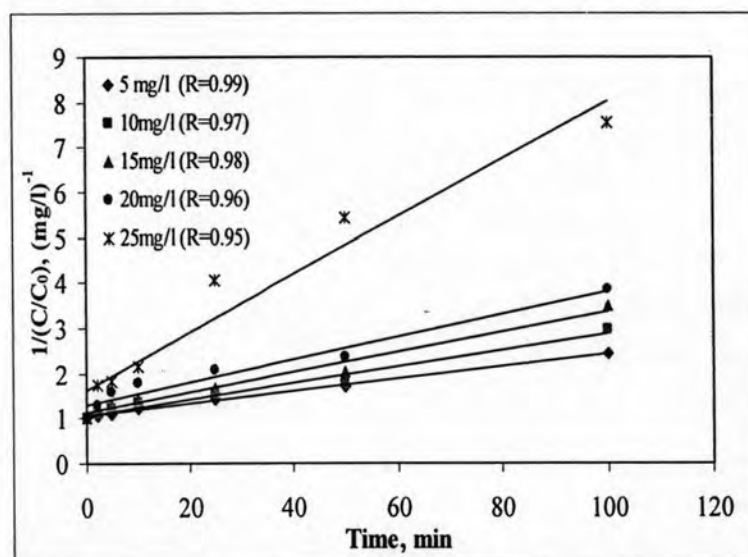


Figure 4.5b Relationship between $1/(C/C_0)$ and time under different Fe^{2+} dosage.

Figure 4.5 Effect of Fe^{2+} concentration on COD removal of RB5; RB5 = 0.1 mM, H_2O_2 = 160 mg/l, carrier = 74.07 g/l, initial pH = 3.

The pseudo-second-order rate constants obtained under different Fe^{2+} concentration are compared in Figure 4.5. It was found that when ferrous dosages increase from 5 to 25 mg/l, the corresponding pseudo-second order rate constants of COD removal increase significantly from 0.020 to 0.213 $(\text{mg/l})^{-1} \text{min}^{-1}$.

Table 4.4 Pseudo-second-order constants of COD removal and %COD removal of reactive dyes under different Fe^{2+} dosage(Appendix C).

Fe^{2+} (mg/l)	Reactive Black 5		Reactive orange 16		Reactive Blue 2	
	$k \times 10^{-2}$ (mg/l) ⁻¹ min ⁻¹	%COD removal	$k \times 10^{-2}$ (mg/l) ⁻¹ min ⁻¹	%COD removal	$k \times 10^{-2}$ (mg/l) ⁻¹ min ⁻¹	%COD removal
5	2.0	67.8	1.4	58.9	0.7	44.9
10	2.8	74.2	1.8	66.3	2.5	71.8
15	3.4	78.1	2.3	71.2	3.8	79.0
20	9.8	91.2	2.5	74.0	4.7	81.7
25	21.3	95.7	6.4	86.7	5.5	84.5

In this study, the target of COD removal efficiency was higher than 80%. Therefore, the Fe^{2+} concentrations were used in the investigation of effect of H_2O_2 on COD removal of reactive dyes; Fe^{2+} 20 mg/l for RB5, Fe^{2+} 25 mg/l for RO16 and Fe^{2+} 20 mg/l for RB2.

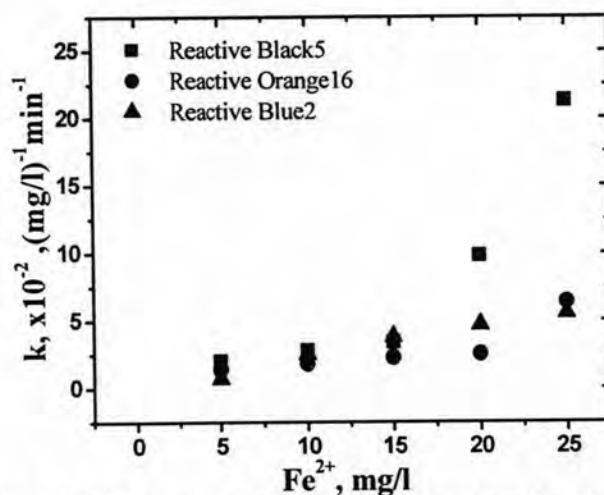


Figure 4.6 Effect of Fe^{2+} concentration on pseudo-second-order constants of COD removal; dyes = 0.1 mM, carrier = 74.07 g/l and initial pH = 3.

4.4.1.2 Effect of H_2O_2 on the COD removal efficiency of reactive dyes

For studying of the effect of H_2O_2 concentration on the COD removal, experiments were conducted by varying its concentrations from 130 to 250 mg/l as shown in Figure 4.8. As mentioned earlier, color of solutions were removed higher than 96% under any condition. For the COD removal, it increased with increasing H_2O_2 concentration. Figure 4.7 and Table 4.5 illustrates the effect of H_2O_2 concentration on the COD removal in terms of k values. The results show that

increasing H_2O_2 concentration did not improve COD removal for all reactive dyes in this investigation because scavenging effect of H_2O_2 on hydroxyl radicals might happen. As reported in the literature, the reaction rate tends to increase with H_2O_2 concentration. However, H_2O_2 not only react to form hydroxyl radicals, but are also scavengers of hydroxyl radicals. Hence it is important to use the optimum H_2O_2 and Fe^{2+} concentration (Parsons, 2004).

Table 4.5 Pseudo-second-order constants of COD removal and %COD removal of reactive dyes under different H_2O_2 dosage (Appendix D).

H_2O_2 (mg/l)	Reactive Black 5		Reactive orange 16		Reactive Blue 2	
	$k \times 10^{-2}$ (mg/l) ⁻¹ min ⁻¹	%COD removal	$k \times 10^{-2}$ (mg/l) ⁻¹ min ⁻¹	%COD removal	$k \times 10^{-2}$ (mg/l) ⁻¹ min ⁻¹	%COD removal
130	2.0	70.7	3.0	76.7	2.2	69.2
160	9.8	91.2	6.4	86.7	4.3	81.7
190	23.2	96.2	3.9	80.2	2.7	74.7
220	30.1	97.1	3.6	78.8	1.5	61.2
250	4.2	83.4	2.3	75.8	1.2	54.6

The results show that the conditions which COD removal efficiency higher than 80% were 20 mg/l Fe^{2+} and 160 mg/l H_2O_2 for RB5, 25 mg/l Fe^{2+} and 160 mg/l H_2O_2 for RO16 and 20 mg/l Fe^{2+} and 160 mg/l H_2O_2 for RB2.

Even though all dyes in this study were reactive dyes, the conditions for remove 80% COD of 0.1 mM reactive dyes are difference. It indicates that Fenton's reagent concentration effect on the reaction depends on the chemical structures of target compounds.

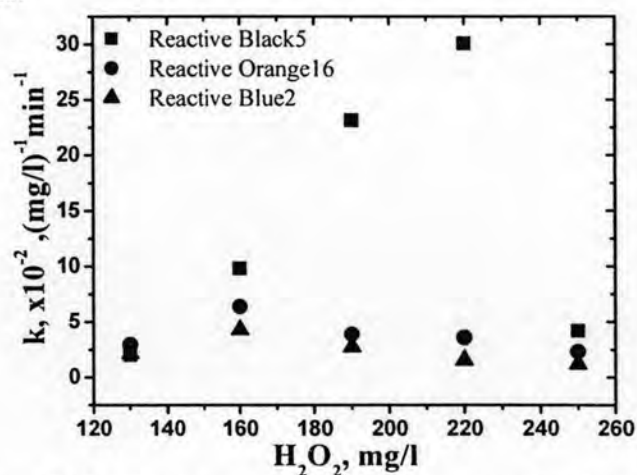


Figure 4.7 Effect of H_2O_2 concentration on pseudo-second-order constants of COD removal; dyes = 0.1 mM, carrier = 74.07 g/l and initial pH = 3.

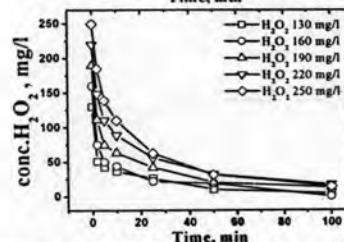
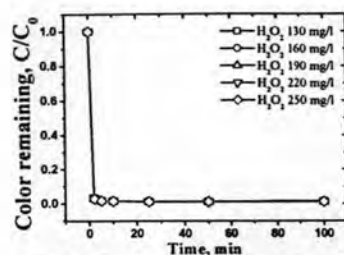
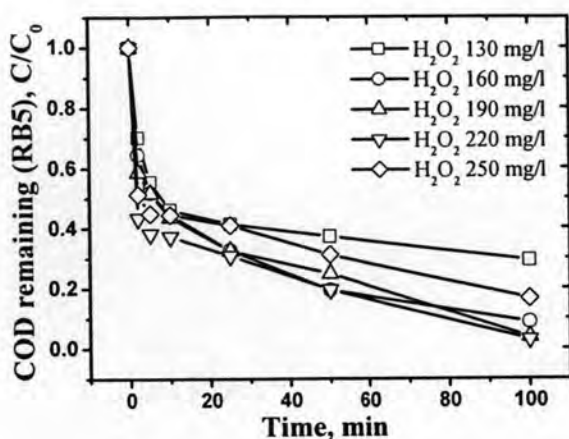


Figure 4.8a Effect of H_2O_2 concentration on COD removal of RB5; RB5 = 0.1 mM, Fe^{2+} = 20 mg/l, carrier = 74.07 g/l, initial pH = 3.

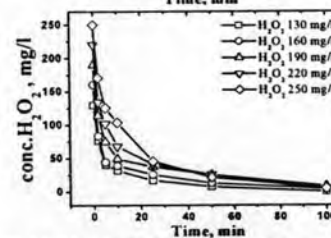
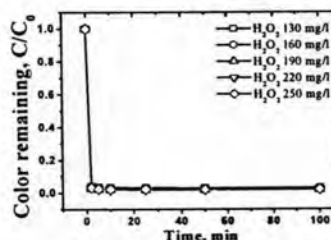
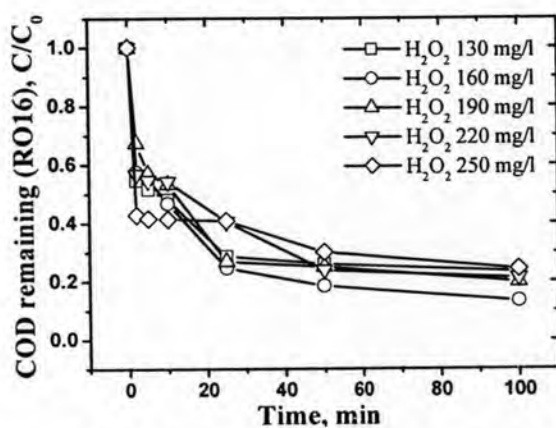


Figure 4.8b Effect of H_2O_2 concentration on COD removal of RO16; RO16 = 0.1 mM, Fe^{2+} = 25 mg/l, carrier = 74.07 g/l, initial pH = 3.

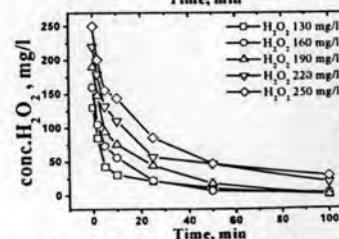
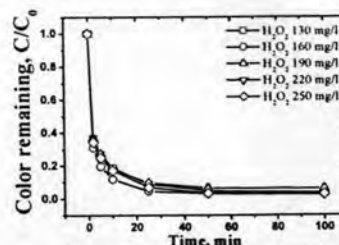
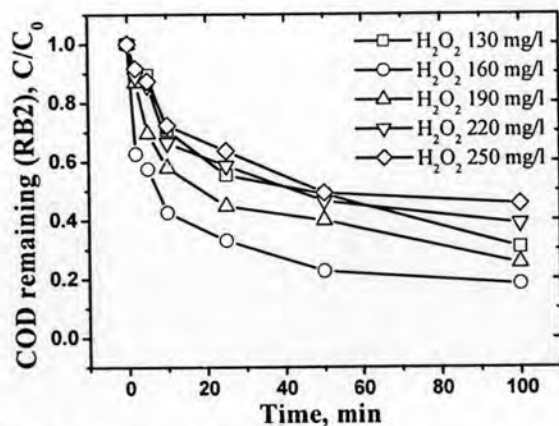


Figure 4.8c Effect of H_2O_2 concentration on COD removal of RB2; RB2 = 0.1 mM, Fe^{2+} = 20 mg/l, carrier = 74.07 g/l, initial pH = 3.

Figure 4.8 Effect of H_2O_2 concentration on COD removal of reactive dyes.

4.4.1.3 Comparison of COD removal efficiency by using the same initial COD values

In this part, COD removal efficiency of reactive dyes by using the same initial COD values was compared in the same condition. Concentration of 0.1 mM reactive dye was used, the initial COD values of reactive black5 (RB5), reactive orange16 (RO16) and reactive blue2 (RB2) are 60 mg/l, 50 mg/l and 60 mg/l, respectively. For comparison of COD removal efficiency by using the same initial COD values, the chosen initial COD value in this study was 60 mg/l. Mixed of 1/3 RB5, 1/3 RO16 and 1/3 RB2 are the mixture reactive dye. Figure 5.8 illustrated the comparison of COD removal efficiency by using the same initial COD values.

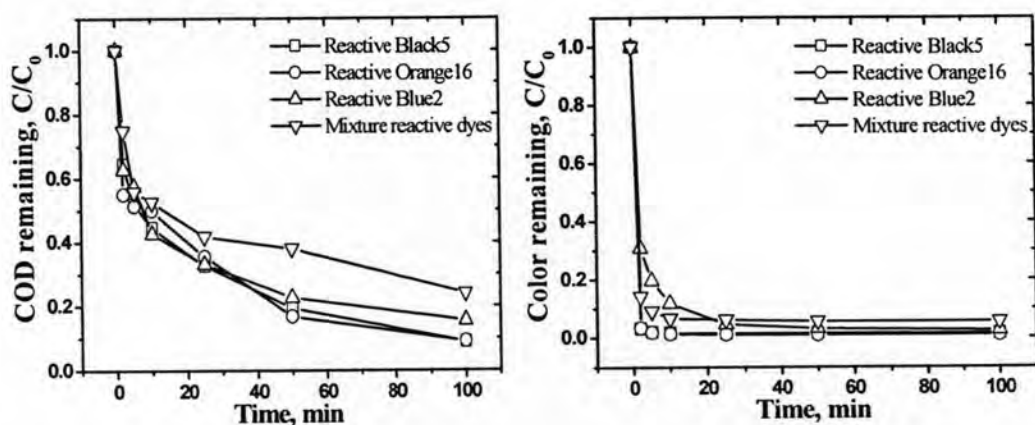


Figure 4.9 Comparison of COD removal efficiency by using the same initial COD values; COD of dyes = 60 mg/l, Fe^{2+} = 20 mg/l, H_2O_2 = 160 mg/l, carrier = 74.07 g/l, initial pH = 3.

Figure 4.9 shown that under the following experiment condition: initial COD of dyes = 60 mg/l, Fe^{2+} = 20 mg/l, H_2O_2 = 160 mg/l, carrier = 74.07 g/l, initial pH = 3, the COD removal of reactive dyes by fluidized-bed Fenton process after 100 minutes reaction time was 91.1%, 91.0%, 84.6% and 75.9% for RB5, RO16, RB2 and mixture reactive dyes, respectively. It was also show that the decolorization of reactive dyes in this condition was 98.7%, 99.2%, 97.6% and 94.5% for RB5, RO16, RB2 and mixture reactive dyes, respectively (Appendix E). And the values of pseudo-second-order reaction rate constant of COD removal were $9.8 \times 10^{-2} \text{ (mg/l)}^{-1} \text{ min}^{-1}$, $9.8 \times 10^{-2} \text{ (mg/l)}^{-1} \text{ min}^{-1}$, $3.2 \times 10^{-2} \text{ (mg/l)}^{-1} \text{ min}^{-1}$ and $2.8 \times 10^{-2} \text{ (mg/l)}^{-1} \text{ min}^{-1}$ for RB5, RO16, RB2 and mixture reactive dyes, respectively .

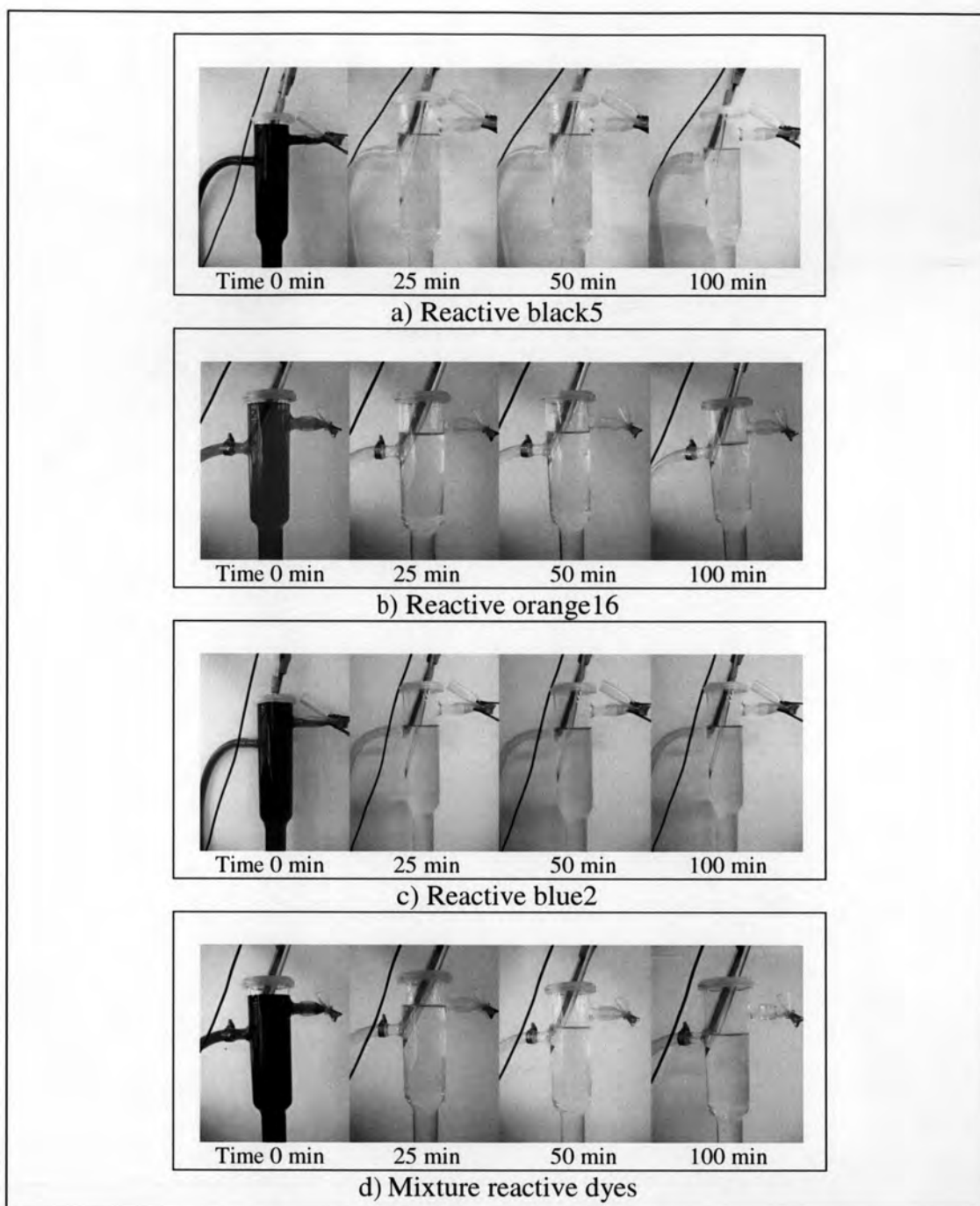


Figure 4.10 Color of synthetic reactive dyes at time interval of 0, 25, 50 and 100 minutes, comparison of COD removal efficiency by using the same initial COD values; COD of dyes = 60 mg/l, Fe^{2+} = 20 mg/l, H_2O_2 = 160 mg/l, carrier = 74.07 g/l, initial pH = 3.

As the results, comparing the COD removal of mixture reactive dyes with the other reactive dyes by using the same initial COD value, COD removal efficiency of the mixture reactive dyes was lower than that of the other dyes. The reason might be due to interaction among three reactive dyes, themselves. Therefore, the structure of

compound in mixture reactive dyes was much more complex and hard to decompose under the same condition.

4.4.2 Color removals of synthetic dyeing wastewater

Due to the part of COD removal of synthetic dyeing wastewater, Fe^{2+} and H_2O_2 concentration was high. Therefore, reaction rate of color removal was too fast. In this part, the color removal rate was investigated, hence, low Fe^{2+} and H_2O_2 concentration was used in this study ($\text{Fe}^{2+} = 1\text{-}5 \text{ mg/l}$, $\text{H}_2\text{O}_2 = 50\text{-}200 \text{ mg/l}$).

4.4.2.1 Effect of Fe^{2+} on the color removal efficiency of reactive dyes

The effects of Fe^{2+} on the color removal of reactive dyes are illustrated in Figure 4.11. The experiments were carried out with $\text{pH} = 3.0$, $\text{H}_2\text{O}_2 = 100 \text{ mg/l}$, $\text{SiO}_2 = 100 \text{ g}$, $\text{Fe}^{2+} = 1 \text{ to } 5 \text{ mg/l}$. The figure reveals that color decreased with time of reaction. Color removal of reactive dyes increased with increasing Fe^{2+} concentration shown in Table 4.6. All of color values for the pseudo-second-order reaction rate constant, k , were calculated from the linear regression of the pseudo-second-order kinetic model with related coefficients higher than 0.98. The rate constants for fluidized-bed Fenton oxidation of reactive dyes are also summarized in Table 4.6 and Figure 4.13. The decolorization of all reactive dyes were higher than 80% by using low ferrous ion concentration but the COD removal efficiency were lower than 50%.

Table 4.6 Pseudo-second-order constants of color removal, %color and %COD removal under different Fe^{2+} dosage; dyes = 0.1 mM, $\text{H}_2\text{O}_2 = 100 \text{ mg/l}$, carrier = 74.07 g/l and $\text{pH} = 3.0$ (Appendix F).

Fe^{2+} (mg/l)	k ($\times 10^{-2}$), ADMI $\text{unit}^{-1} \text{min}^{-1}$	%Color removal	%COD removal
Reactive black 5			
1	12.0	92.6	30.0
2	24.9	96.3	31.2
3	111.7	99.1	33.7
Reactive orange 16			
1	32.1	96.9	10.7
2	104.3	99.0	40.6
3	143.8	99.3	46.8
Reactive blue 2			
1	4.5	80.9	12.0
2	5.2	83.6	14.6
3	5.3	84.2	15.6
4	15.2	94.2	31.9
5	24.2	96.2	48.7

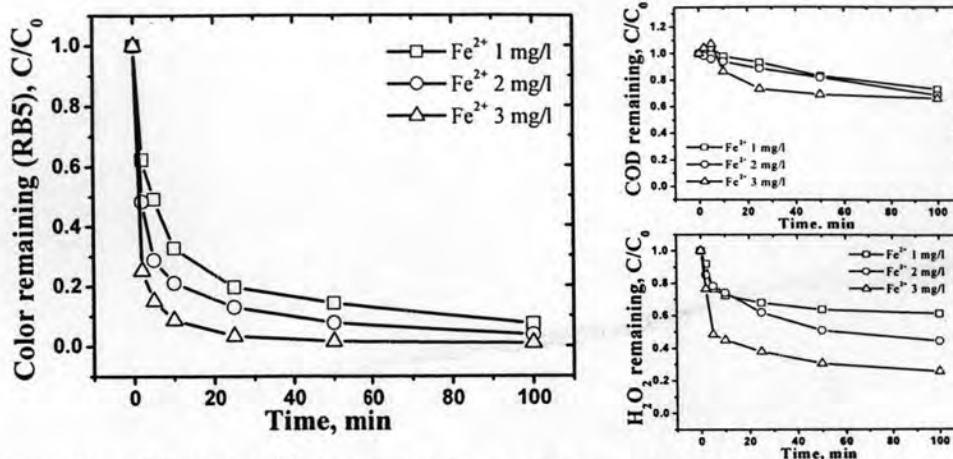


Figure 4.11a Effect of Fe^{2+} concentration on color removal of RB5; RB5 = 0.1 mM, $\text{H}_2\text{O}_2 = 100 \text{ mg/l}$, carrier = 74.07 g/l, initial pH = 3.

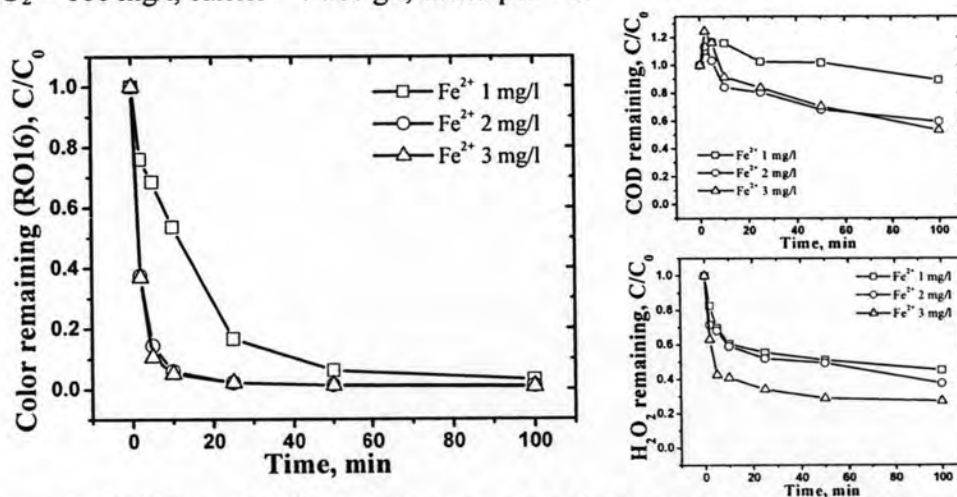


Figure 4.11b Effect of Fe^{2+} concentration on COD removal of RO16; RO16 = 0.1 mM, $\text{H}_2\text{O}_2 = 100 \text{ mg/l}$, carrier = 74.07 g/l, initial pH = 3.

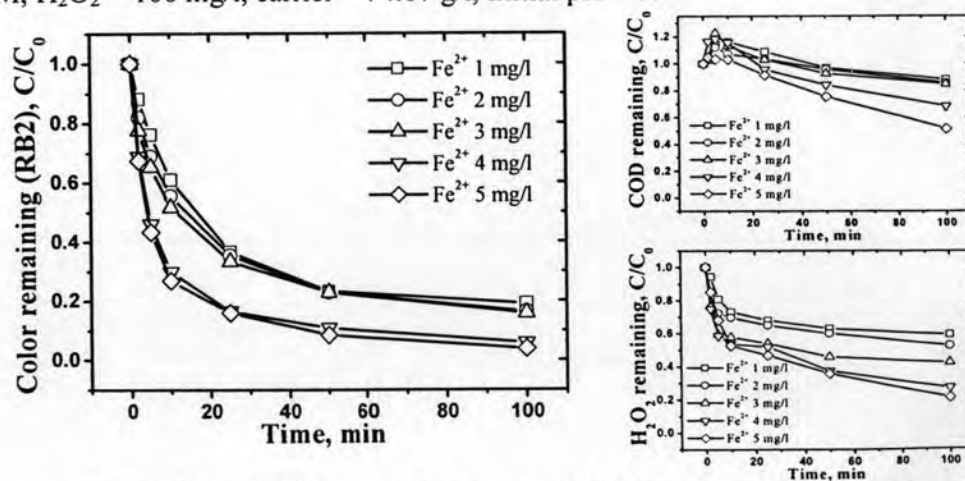


Figure 4.11c Effect of Fe^{2+} concentration on COD removal of RB2; RB2 = 0.1 mM, $\text{H}_2\text{O}_2 = 100 \text{ mg/l}$, carrier = 74.07 g/l, initial pH = 3.

Figure 4.11 Effect of Fe^{2+} concentration on color removal of reactive dyes.

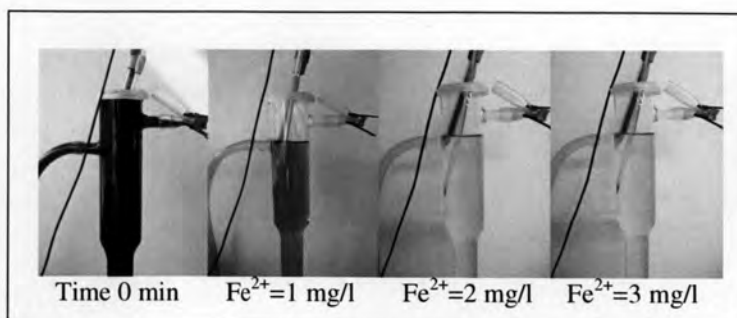


Figure 4.12a Effect of Fe^{2+} concentration on color removal of reactive dyes at 100 minutes; RB5 = 0.1 mM, H_2O_2 = 100 mg/l, carrier = 74.07 g/l, initial pH = 3.

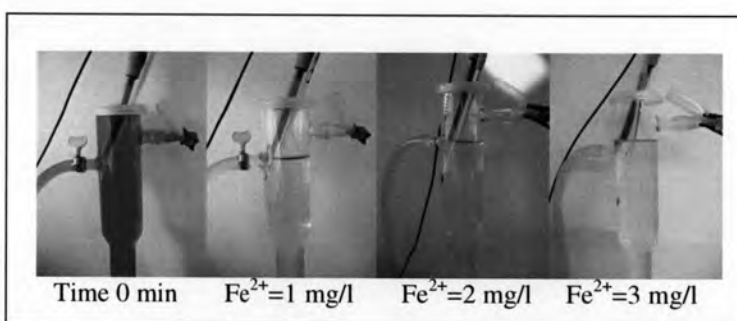


Figure 4.12b Effect of Fe^{2+} concentration on color removal of reactive dyes at 100 minutes; RO16 = 0.1 mM, H_2O_2 = 100 mg/l, carrier = 74.07 g/l, initial pH = 3.

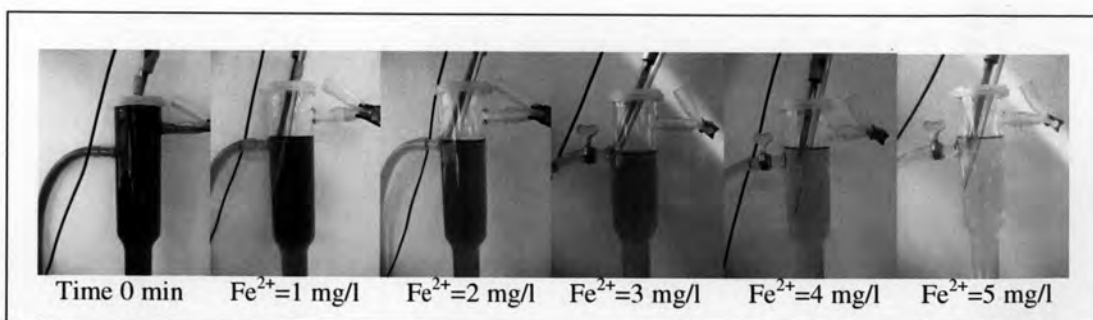


Figure 4.12c Effect of Fe^{2+} concentration on color removal of reactive dyes at 100 minutes; RB2 = 0.1 mM, H_2O_2 = 100 mg/l, carrier = 74.07 g/l, initial pH = 3.

Figure 4.12 Effect of Fe^{2+} concentration on color removal of reactive dyes at 100 minutes.

Concentration of 0.1 mM reactive dye was used, the initial color values of reactive black5 (RB5), reactive orange16 (RO16) and reactive blue2 (RB2) are 6500 ADMI units, 5100 ADMI units and 3000 ADMI units, respectively. Target remaining color values for all reactive in this study was less than 400 ADMI units due to the discharge standards of 1998, textile industries are required by Environmental Protection Administration of Taiwan to comply with the color less than 400 in American Dye Manufacturer Institute (ADMI) unit. (Environmental Protection Administration, ROC., 1998).

As the results, at initial pH 3, dyes 0.1 mM, H_2O_2 100 mg/l, carrier 74.07 g/l, Fe^{2+} concentrations 2 mg/l for RB5, 1 mg/l for RO16 and 4 mg/l for RB2, the color remaining was less than discharge standard of Taiwan. Therefore, these Fe^{2+} concentrations were chosen in the experiments of effect of H_2O_2 on the color removal efficiency of reactive dyes.

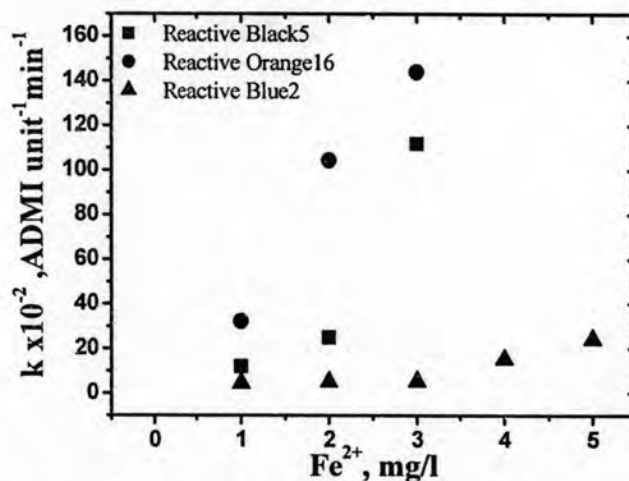


Figure 4.13 Effect of Fe^{2+} concentration on pseudo-second-order constants; dyes = 0.1 mM, H_2O_2 = 100 mg/l, carrier = 74.07 g/l and initial pH = 3.

In this part, the COD value of synthetic dyes seemed to slightly increase after reaction started within 5 minutes under the condition with low Fe^{2+} concentration. The reason might be that the complex bonds of reactive dye was broken down due to the attacked from Fenton's reaction, yielding higher COD detectability. Moreover, under this low Fe^{2+} concentration, complete oxidation of reactive dye by Fenton's reaction could not yet be highly achieved. Comparing to the condition with high Fe^{2+} concentration,

COD value decreased continuously since more complete oxidation by Fenton's reaction could be highly obtained.

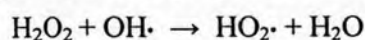
4.4.2.2 Effect of H₂O₂ on the color removal efficiency of reactive dyes

Table 4.7, Figure 4.14 and Figure 4.15 show the pseudo-second-order constants for color removal, %color removal and %COD removal of reactive dyes. Apparently, when the H₂O₂ concentration increased, the decolorization of reactive dyes was enhanced because more Fe²⁺ and OH· are formed at higher H₂O₂ concentrations in solution. However, when the H₂O₂ concentration was higher than a specific level, the degradation rate of reactive dyes slightly slows down.

Table 4.7 Pseudo-second-order constants of color removal, %color and %COD removal under different H₂O₂ dosage (Appendix G).

H ₂ O ₂ (mg/l)	k (x 10 ⁻²) ,ADMI unit ¹ min ⁻¹	%Color removal	%COD removal
Reactive black 5			
50	11.0	92.2	18.0
100	24.9	96.3	31.2
150	32.9	97.2	34.1
200	24.3	96.2	32.3
Reactive orange 16			
50	13.6	93.0	4.7
100	32.1	96.9	14.1
150	25.8	96.2	13.4
200	25.2	96.2	3.7
Reactive blue 2			
50	5.9	85.5	11.1
100	15.9	94.2	31.9
150	22.0	95.7	30.7
200	23.4	96.0	37.9

This can be explained by the so-called scavenging effect. Generally, the degradation rate of organic compounds increases as the H₂O₂ concentration increases until a critical H₂O₂ concentration is achieved. The reaction of H₂O₂ and OH· in aqueous solution can be expressed by the following Equation (2-8) (Parsons, 2004):



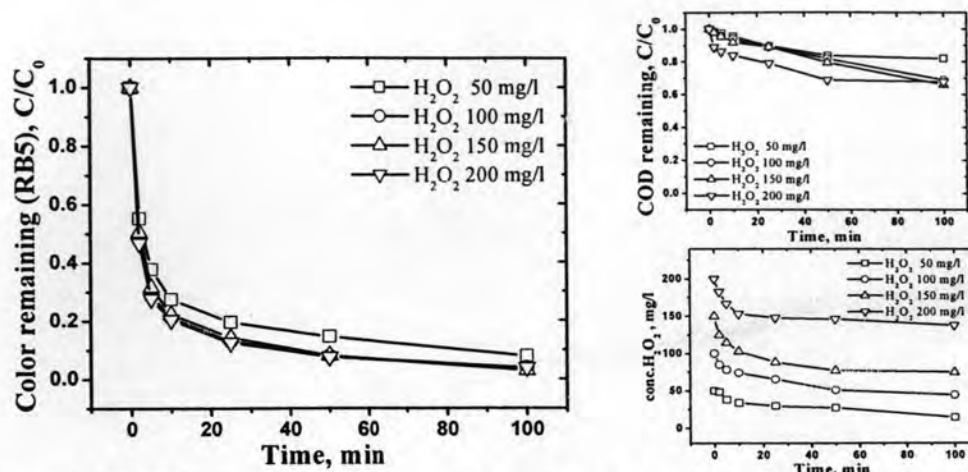


Figure 4.14a Effect of H₂O₂ concentration on color removal of RB5; RB5 = 0.1 mM, Fe²⁺ = 2 mg/l, carrier = 74.07 g/l, initial pH = 3.

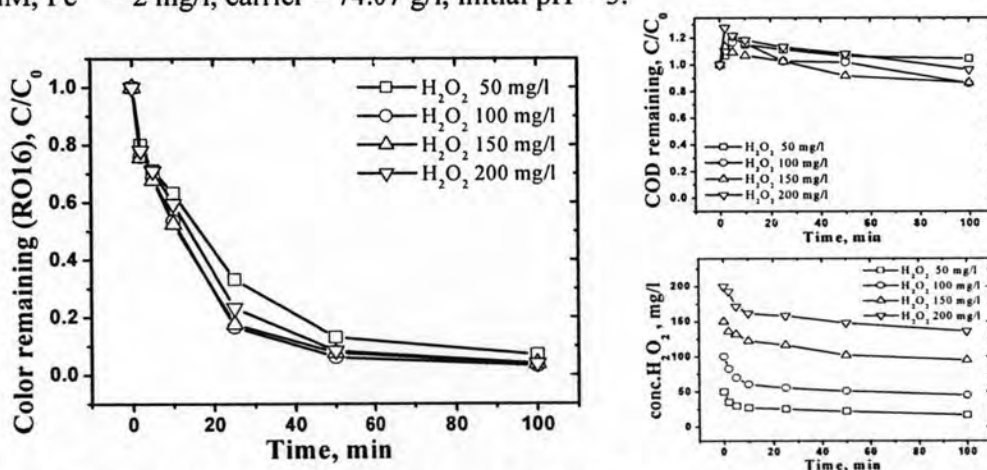


Figure 4.14b Effect of H₂O₂ concentration on color removal of RO16; RO16 = 0.1 mM, Fe²⁺ = 1 mg/l, carrier = 74.07 g/l, initial pH = 3.

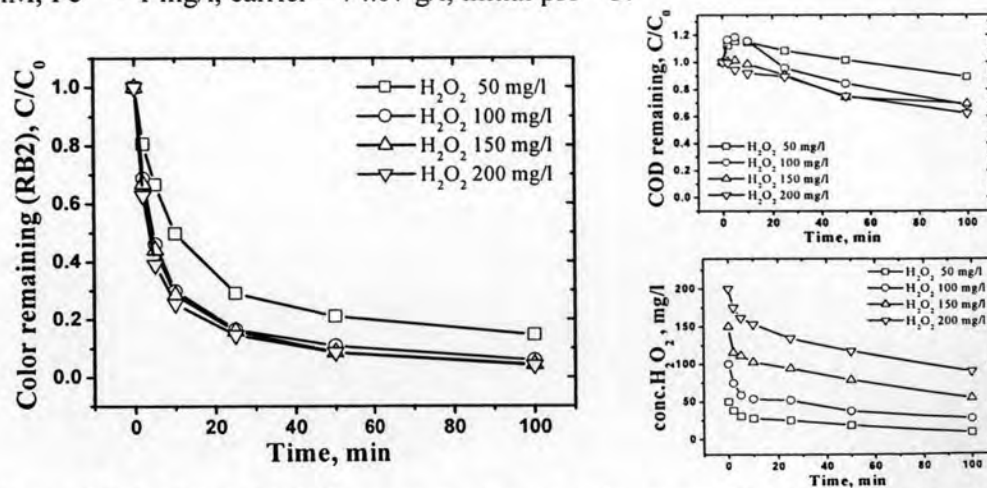


Figure 4.14c Effect of H₂O₂ concentration on color removal of RB2; RB2 = 0.1 mM, Fe²⁺ = 4 mg/l, carrier = 74.07 g/l, initial pH = 3.

Figure 4.14 Effect of H₂O₂ concentration on color removal of reactive dyes.

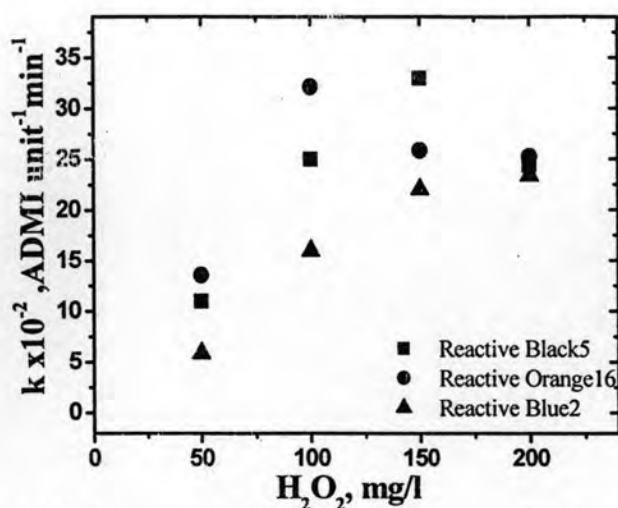


Figure 4.15 Effect of H₂O₂ concentration on pseudo-second-order constants; dyes = 0.1 mM, carrier = 74.07 g/l and initial pH = 3.

The results show that the conditions which color less than 400 in ADMI units were 2 mg/l Fe²⁺ and 100 mg/l H₂O₂ for RB5, 1 mg/l Fe²⁺ and 50 mg/l H₂O₂ for RO16 and 4 mg/l Fe²⁺ and 100 mg/l H₂O₂ for RB2.

The hydroxyl free radical generated would attack the unsaturated dye molecules and the azo bond (N=N) in the chromophore or chromogen, thus decolorizing the wastewater. The rate of the oxidation reaction depends on the concentration of hydroxyl free radical, reaction conditions and pH (Pignatello, cited in Swaminathan et al., 2003: 620). Deng et al., cited in Swaminathan et al. (2003) reported that the decolorization of reactive dyes by photo-Fenton system was dependent on the molecular structure of the dyes that is the same as this study.

The color removal was easier than the COD removal indicating that the chromophoric groups were destroyed during the degradation of dyes, and were partly mineralized to CO₂ and H₂O. Although the chromophoric structures of the dye molecules are destroyed by hydroxyl radicals, some colorless degradation intermediates are formed in solution during the reaction. In most cases, adjacent aromatic ring structure is one of the intermediates (Kang et al., cited in Xu et al., 2004: 597).

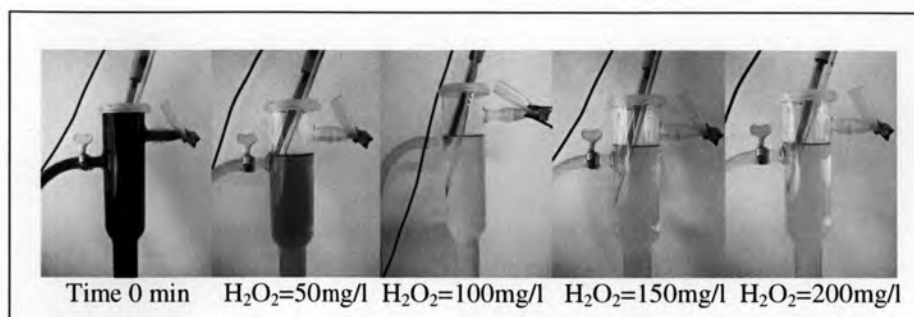


Figure 4.16a Effect of H_2O_2 concentration on color removal of reactive dyes at 100 minutes; RB5 = 0.1 mM, Fe^{2+} = 2 mg/l, carrier = 74.07 g/l, initial pH = 3.

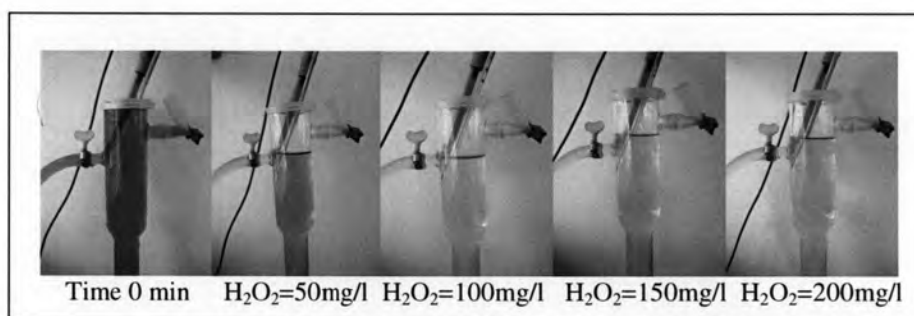


Figure 4.16b Effect of H_2O_2 concentration on color removal of reactive dyes at 100 minutes; RO16 = 0.1 mM, Fe^{2+} = 1 mg/l, carrier = 74.07 g/l, initial pH = 3.

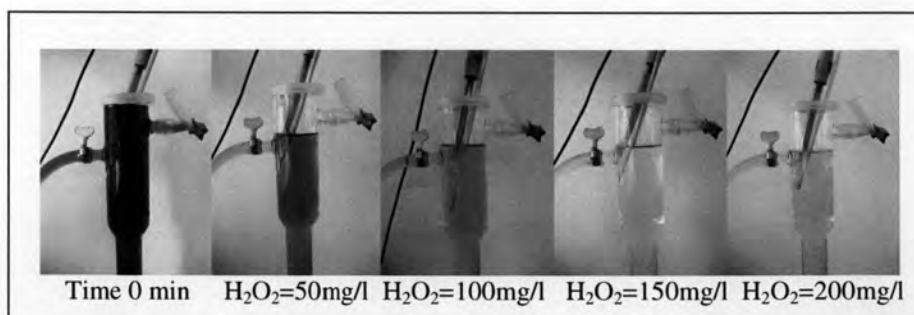


Figure 4.16c Effect of H_2O_2 concentration on color removal of reactive dyes at 100 minutes; RB2 = 0.1 mM, Fe^{2+} = 4 mg/l, carrier = 74.07 g/l, initial pH = 3.

Figure 4.16 Effect of H_2O_2 concentration on color removal of reactive dyes at 100 minutes.

4.4.2.3 Color removal kinetic for fluidized-bed Fenton process

The oxidation of reactive dyes in the Fenton's reaction obeys a second-order behavior. It was found that the value of rate constant, k , increases with increasing Fenton's reagent concentration. It is important to mention that kinetic determination in this section was performed which obtained from the previous sections.

4.4.2.3.1 Effect of Fe^{2+}

From the results of previous section, Fenton's reagent concentration effect on the reaction depends on the chemical structures of target compounds. And in this study, the three reactive dyes were used, therefore, the color removal kinetics of three reactive dyes were different.

The kinetic determination of reactive dyes was performed based on the condition; RB5 = 0.1 mM, H_2O_2 = 100 mg/l, carrier = 74.07 g/l, initial pH = 3.

As shown in Figure 4.17, relationship between color removal rate constant and initial Fe^{2+} concentration, the value of rate constant, k_F , increases with the increase in initial Fe^{2+} concentration. Therefore, the pseudo-second-order rate constants in terms of initial Fe^{2+} concentration are obtained as:

$$\text{Reactive black5: } k_F = 0.10 [\text{Fe}^{2+}]^{1.9}$$

$$\text{Reactive orange16: } k_F = 0.34 [\text{Fe}^{2+}]^{1.4}$$

$$\text{Reactive blue2: } k_F = 0.04 [\text{Fe}^{2+}]^{1.1}$$

where k_F is the Fe^{2+} rate constant.

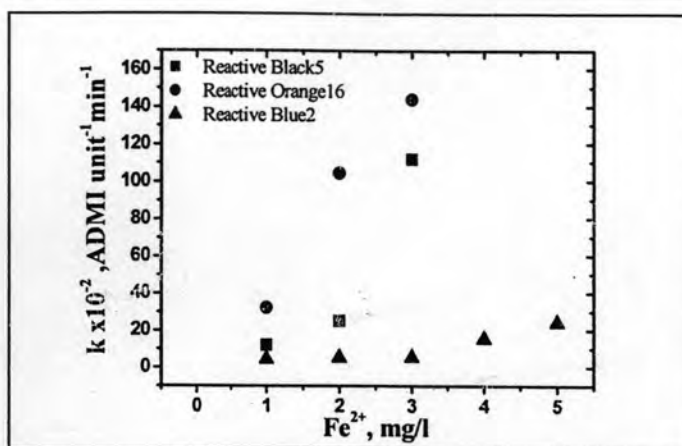


Figure 4.17a Relationship between color removal rate constant and initial Fe^{2+} concentration in normal scale

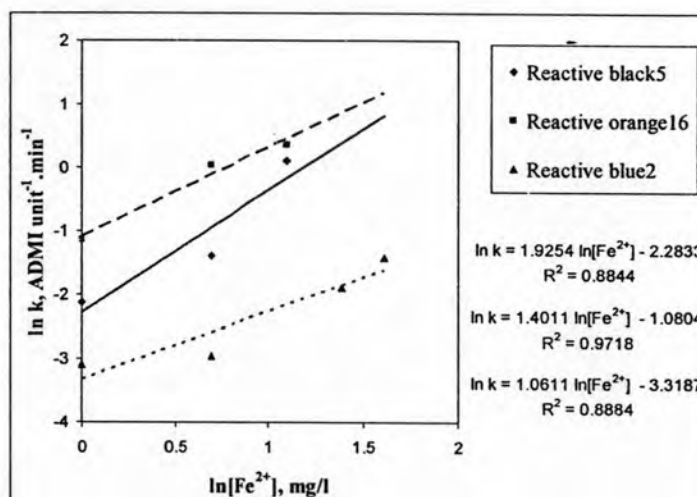


Figure 4.17b Relationship between color removal rate constant ($\ln k$) and initial Fe^{2+} concentration ($\ln[Fe^{2+}]$) in normal scale

Figure 4.17 Relationship between color removal rate constant and initial Fe^{2+} concentration; dyes = 0.1 mM, H_2O_2 = 100 mg/l, carrier = 74.07 g/l and initial pH = 3.

4.4.2.3.1 Effect of H_2O_2

Color removal efficiency increased considerably as the H_2O_2 increased from 50 mg/l to 200 mg/l. From the Figure 4.18, it can be seen that initial concentration of H_2O_2 is a function of reactive dye oxidation. In this case the relationship of k_H and H_2O_2 concentration is can be expressed by equation as:

$$\text{Reactive black5 : } k_H = 2.1 \times 10^{-3} [H_2O_2]^{1.0}$$

$$\text{Reactive blue2 : } k_H = 0.5 \times 10^{-3} [H_2O_2]^{1.2}$$

where k_H is the H_2O_2 rate constant.

For this part, the relationship of k_H and H_2O_2 concentration can not be found under the condition; $H_2O_2 = 50\text{--}200$ mg/l, due to under this condition, the linear model from the relationship of k_H and H_2O_2 concentration was not good fit. Due to when the H_2O_2 concentration was higher than 100 mg/l, the color removal efficiency decreased by scavenging effect.

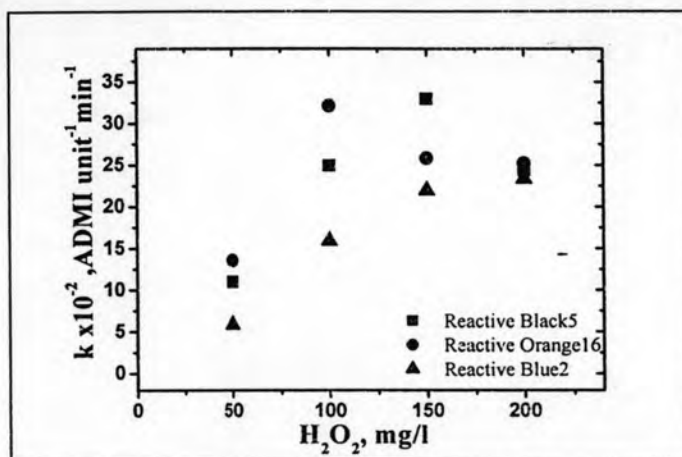


Figure 4.18a Relationship between color removal rate constant and initial H_2O_2 concentration in normal scale

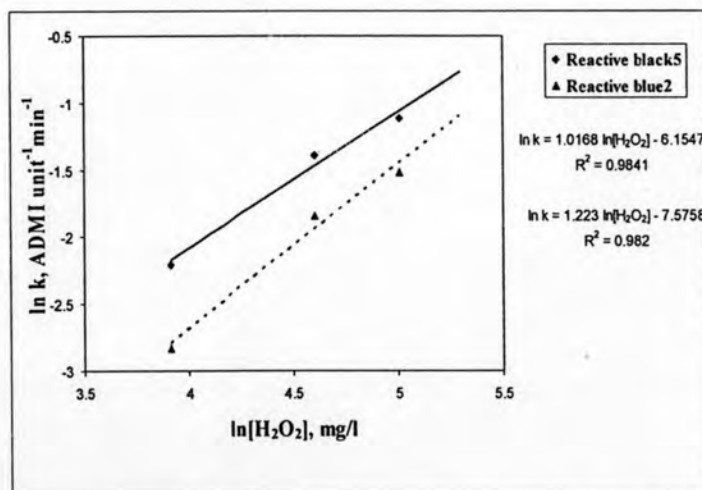


Figure 4.18b Relationship between color removal rate constant ($\ln k$) and initial H_2O_2 concentration ($\ln[H_2O_2]$) in normal scale

Figure 4.18 Relationship between color removal rate constant and initial H_2O_2 concentration; dyes = 0.1 mM, carrier = 74.07 g/l and initial pH = 3.

After all individual reaction order with respect to each reactants were known, the overall rate equation for color removal of reactive dyes by fluidized-bed Fenton process can be written as:

$$\text{Reactive black5: } k_{\text{obs}} = 2 \times 10^{-4} [\text{Fe}^{2+}]^{1.9} [\text{H}_2\text{O}_2]^{1.0}$$

$$\text{Reactive blue2: } k_{\text{obs}} = 2 \times 10^{-5} [\text{Fe}^{2+}]^{1.1} [\text{H}_2\text{O}_2]^{1.2}$$

where k_{obs} is the bi-factor rate constant.

This rate equation is valid under the experimental conditions as follows: dyes = 0.1 mM, carrier = 74.07 g/l, initial Fe^{2+} = 1-5 mg/l, initial H_2O_2 = 50-200 mg/l and pH = 3 at room temperature.

4.4.2.4 Comparison of color removal efficiency by using the same initial color values

For comparison of color removal efficiency by using the same initial color values, the chosen initial color value in this study was 6500 in ADMI units. The concentration of each dyes were calculated by using the dyes calibration curve (Appendix N). Figure 4.19 shown the comparison of color removal efficiency by using the same initial color values.

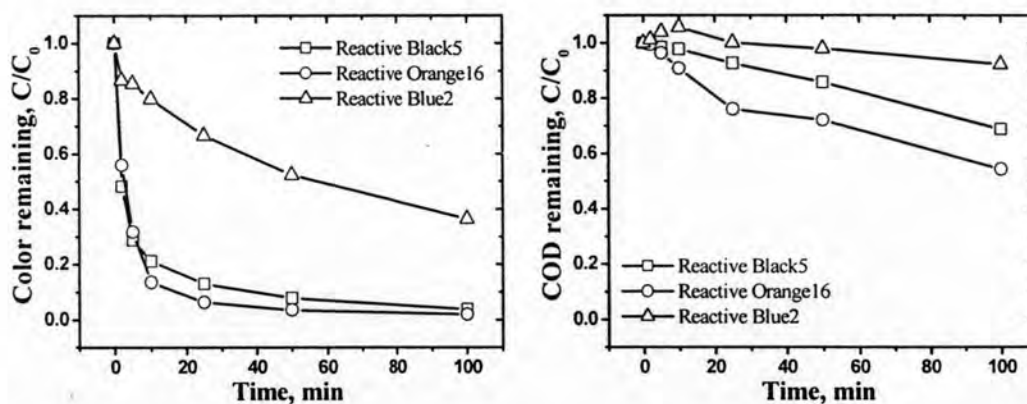


Figure 4.19 Comparison of color removal efficiency by using the same initial color values; color of dyes = 6500 ADMI units, Fe^{2+} = 2 mg/l, H_2O_2 = 100 mg/l, carrier = 74.07 g/l, initial pH = 3.

Figure 4.19 shown that under the following experiment condition; initial color of dyes = 6500 ADMI units, Fe^{2+} = 2 mg/l, H_2O_2 = 100 mg/l, carrier = 74.07 g/l, initial pH = 3, the color removal of reactive dyes by fluidized-bed Fenton process

after 100 minutes reaction time was 96.3%, 98.1% and 63.65% for RB5, RO16 and RB2, respectively.

It was also show that the COD removal efficiency of reactive dyes in this condition was 31.2%, 45.7% and 7.8% for RB5, RO16 and RB2, respectively (Appendix H). And the values of pseudo-second-order reaction rate constant of color removal were 11.4×10^{-2} $\text{ADMlunit}^{-1}\text{min}^{-1}$, 28.3×10^{-2} $\text{ADMlunit}^{-1}\text{min}^{-1}$ and 0.9×10^{-2} $\text{ADMlunit}^{-1}\text{min}^{-1}$ for RB5, RO16 and RB2, respectively.

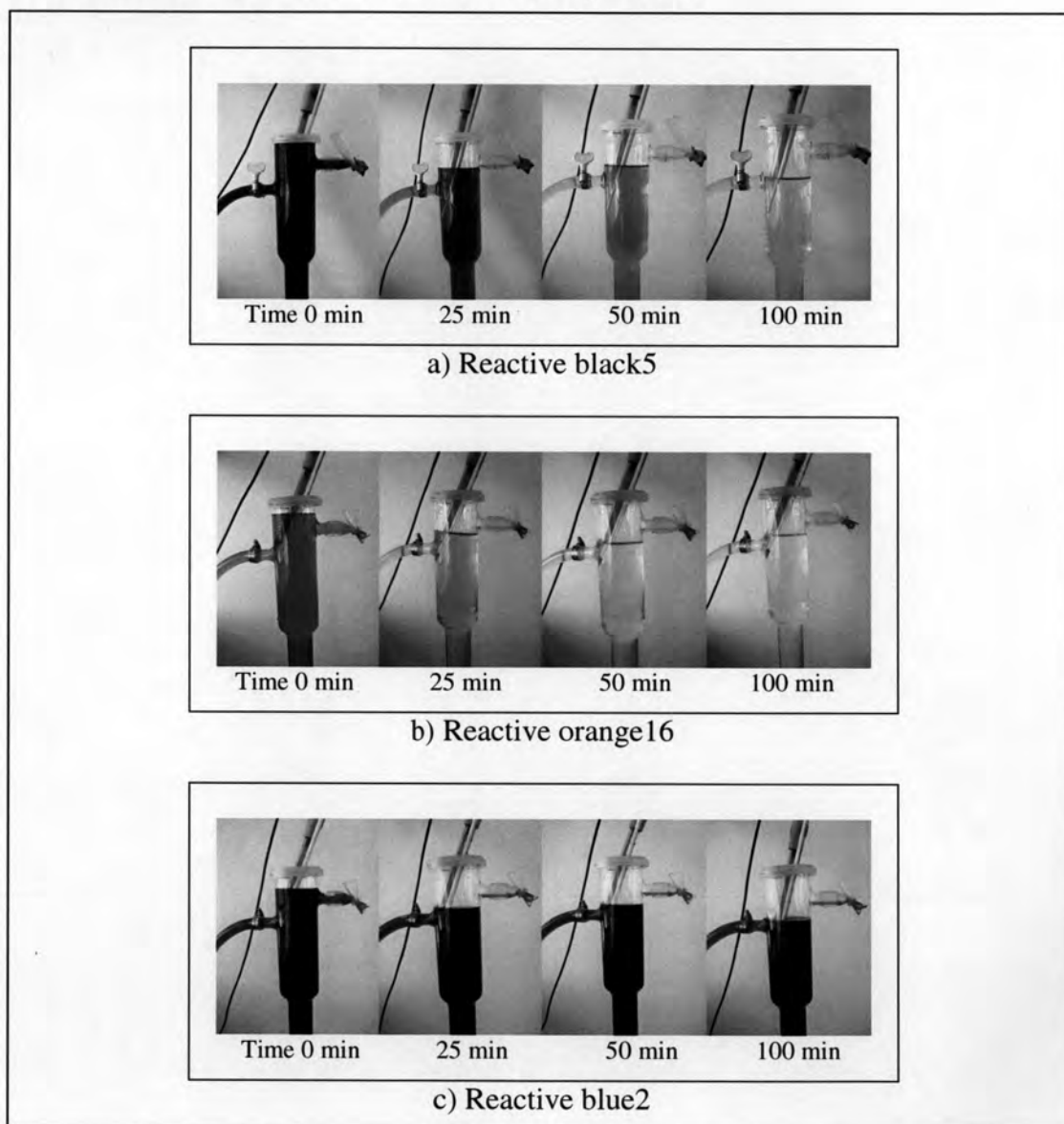
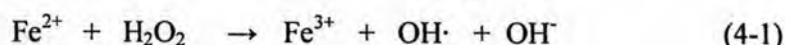


Figure 4.20 Color of synthetic reactive dyes at time interval of 0, 25, 50 and 100 minutes, comparison of color removal efficiency by using the same initial color values; color of dyes = 6500 ADMl units, Fe^{2+} = 2 mg/l, H_2O_2 = 100 mg/l, carrier = 74.07 g/l, initial pH = 3.

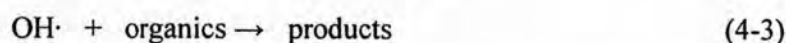
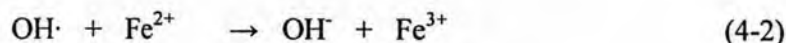
As the results of comparison of COD and color removal efficiency by using the same initial COD value and the same initial color value, the sequence of COD and color removal efficiency for synthetic reactive dyes was RO16 > RB5 > RB2.

Although initial COD and color value of reactive dyes in this study were all the same, the COD and color removal efficiency were still difference at the same condition. Therefore, it indicated that Fenton's reagent concentration effect on the reaction depends on the chemical structures of target compounds.

From the above results of COD and color removals of synthetic dyeing wastewater can be concluded that the Fenton system uses Fe^{2+} to react with H_2O_2 , producing hydroxyl radicals with powerful oxidizing abilities to degrade certain toxic contaminants (Parsons, 2004):

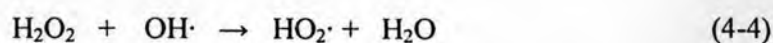


Because the added amount of Fe^{2+} directly influenced the production of hydroxyl radicals, it has a large influence on the decomposition rate of reactive dyes. The reaction rate increased with increasing Fe^{2+} concentration. But hydroxyl radicals may react with Fe^{2+} to form Fe^{3+} or react with organics (Lu et al., 1999):



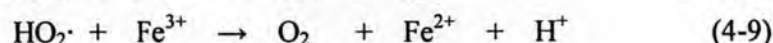
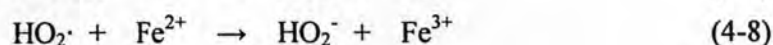
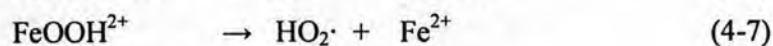
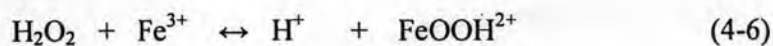
In this study, oxidation of synthetic reactive dyes did not be inhibited by increasing the concentration of Fe^{2+} . The reason could be that the amounts of Fe^{2+} added in these experiments have not yet reached the degree of inhibition.

Generally, the degradation rate of organic compounds increases as the H_2O_2 concentration increases until a critical H_2O_2 concentration is achieved. However, when a concentration higher than the critical concentration is used, the degradation rate of organic compounds will decrease as a result of the so-called scavenging effect (Hsueh et al., 2005):



These two reactions reduced the probability of organic compounds attacked by hydroxyl radicals, and cause the oxidation rate of reactive dyes to drop.

Ferrous ions and radicals are produced during the reactions. The reactions are as shown in Eqs. (4-6)-(4-9) (Walling, cited in Lu et al., 1999: 278).



The reaction rate in Eq. (4-6) is much slower than that in Eq. (4-1). It is derived that Fe^{2+} are consumed quickly, but reproduced slowly. Consequently, the oxidation rate of organic compounds is fast when large amount of Fe^{2+} are present because large amount of hydroxyl radicals are produced. However, the Fenton reaction may slow down due to the slow Fe^{2+} production.

4.4.3 COD and color removals of synthetic commercial dyeing wastewater

Due to the COD and color removal of industrial wastewater was studied in the next scenario, therefore, the commercial dyes which were used in textile industrial, was investigated in this part. For the synthetic reactive dyes, COD values of concentration 0.1 mM of reactive dyes were very low (50-60 mg/l) and color values were very high (3000-6500 ADMI units), the results show that dye decolorization can occur at very low iron concentrations (1-5 mg/l) in fluidized-bed Fenton reactions. But the dyeing wastewater from textile factory was opposite, the COD value was higher and color value was lower.

Therefore, the commercial dyes were consequently used in this study for investigated that the commercial dyes were also easy to remove the color as the reactive dyes with reagent grade. The commercial dyes were taken from the textile factory (Nan-Yuan Industrial Co., Ltd, Tainan, Taiwan). Molecular weight of commercial dyes was unknown, the used concentration was 100 mg/l under the condition: $\text{Fe}^{2+} = 20$ mg/l, $\text{H}_2\text{O}_2 = 160$ mg/l, carrier = 74.07 g/l and initial pH = 3.

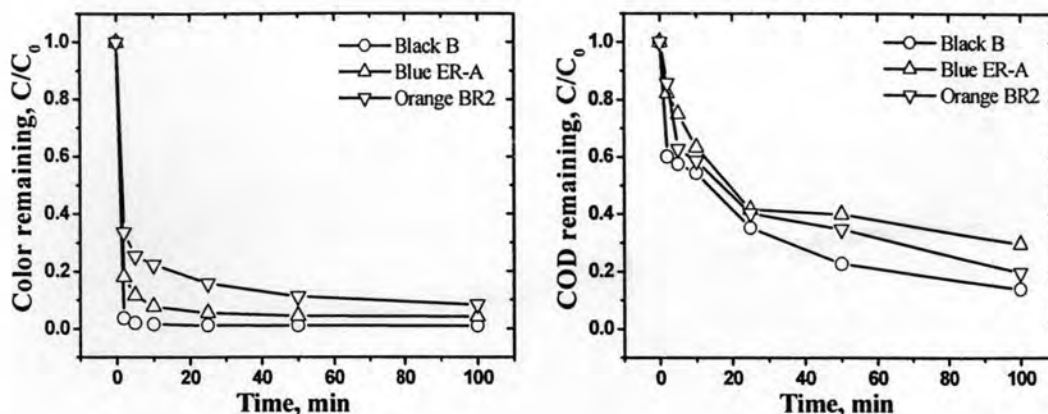


Figure 4.21 COD and color removals of synthetic commercial dyeing wastewater; dyes =100 mg/l, Fe^{2+} =20 mg/l, H_2O_2 =160 mg/l, carrier =74.07 g/l and initial pH= 3.

Table 4.8 Initial COD and color, %COD and %color removal efficiency of commercial dyes (Appendix I).

Dyes	COD			Color		
	Initial COD (mg/l)	Final COD (mg/l)	%COD removal	Initial color (ADMI units)	Final color (ADMI units)	%color removal
Black B	55	7.6	86.1	6700	74	98.9
Blue ER-A	57	16.9	70.3	5100	212	95.8
Orange BR2	108	21.4	80.2	4600	384	91.6

Figure 4.21 and Table 4.8 illustrated that although the target compounds were commercial dyes, %COD and color removal efficiency were also as high as these of reactive dyes with reagent grade. Both reactive dyes with reagent grade and commercial dyes, initial COD was low but initial color was high. And it can be easy to remove by fluidized-bed Fenton process. It indicated that majority high COD in industrial wastewater from other chemical not dyes. Therefore, industrial wastewater should be used higher Fenton's reagent concentration.

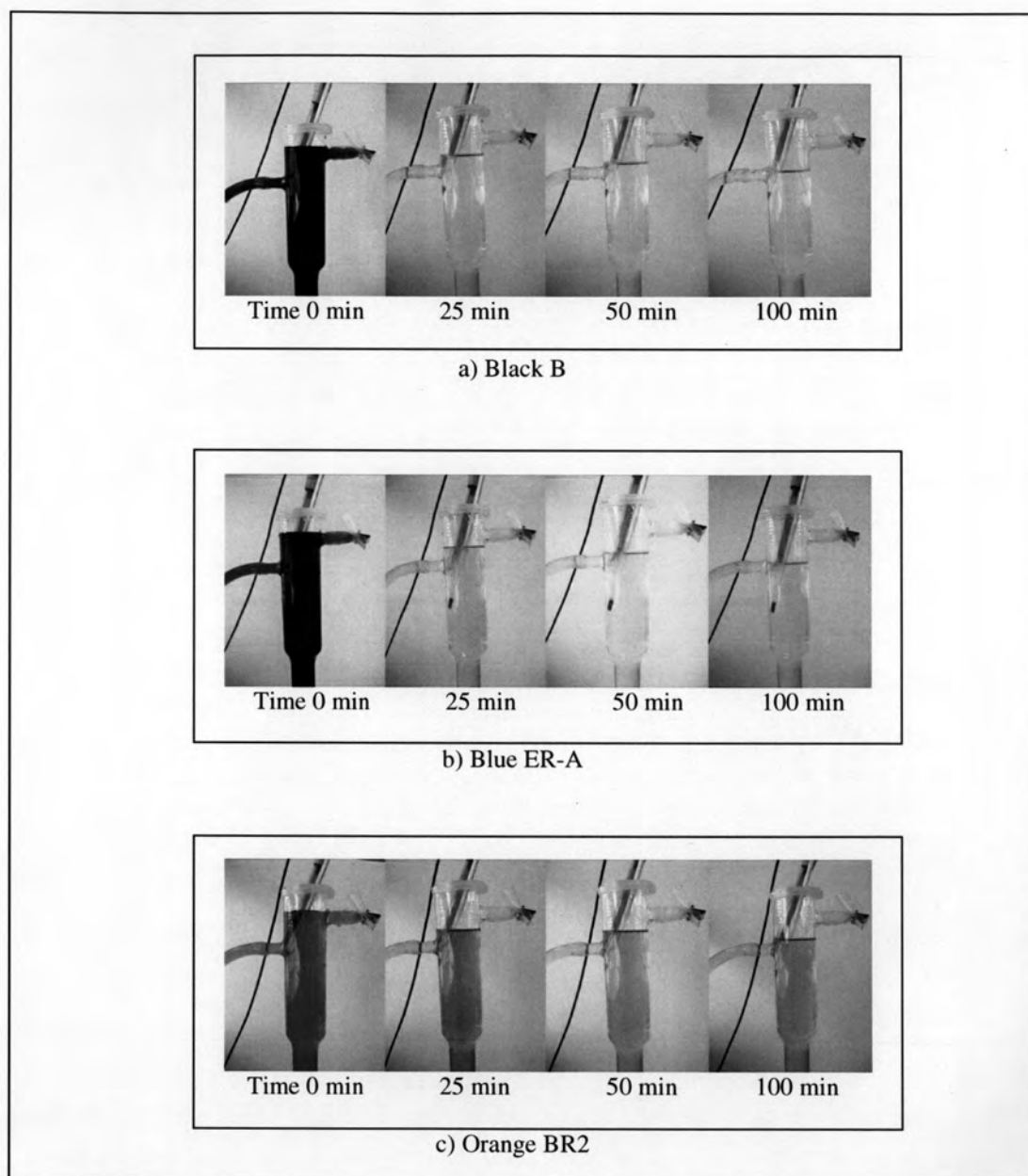


Figure 4.22 Color of synthetic commercial reactive dyes at time interval of 0, 25, 50 and 100 minutes; dyes =100 mg/l, Fe^{2+} =20 mg/l, H_2O_2 =160 mg/l, carrier =74.07 g/l and initial pH= 3.

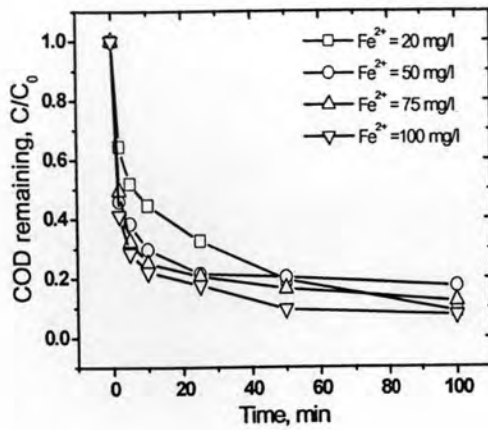
4.4.4 Iron crystallization

From the previous experiments, Fe^{2+} concentration used was low (1-25 mg/l). Therefore, after 100 minutes, the iron remaining in the solution was slightly decreased. In this part, the higher Fe^{2+} concentration was used to determine the impact of crystallized iron that coating onto the surface of silica oxide (SiO_2) in fluidized-bed Fenton process with the condition: $\text{RB5} = 0.1 \text{ mM}$, $\text{Fe}^{2+} = 20\text{-}100 \text{ mg/l}$, $\text{H}_2\text{O}_2 = 160 \text{ mg/l}$, carrier = 74.07 g/l, initial pH = 3. The higher Fe^{2+} concentration was used in this study for investigating as a continuous mode. It was found that there was difference regarding on the iron crystallization among Fe^{2+} concentration 20 mg/l to 100 mg/l.

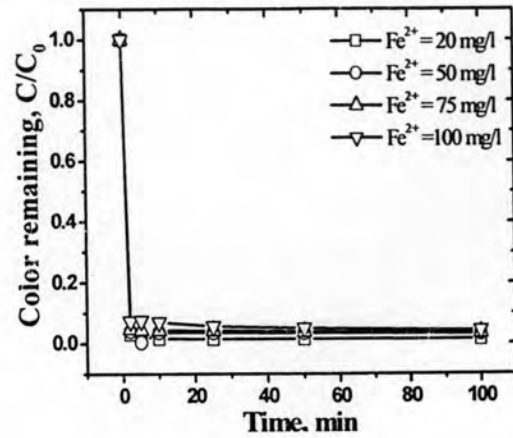
At the condition with high Fe^{2+} concentration, the total iron remaining was lower than that at condition with low Fe^{2+} concentration. The total iron remaining in the solution was lower that means iron in the solution transformed into iron oxide (FeOOH) onto the carrier surface via the crystallization. Therefore, this process combines the functions of homogeneous chemical oxidation ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$), heterogeneous chemical oxidation ($\text{H}_2\text{O}_2/\text{FeOOH}$), fluidized-bed crystallization, and reductive dissolution of FeOOH . This process not only attains high COD removal efficiency but also reduces the large amount of iron sludge being produced. Furthermore, FeOOH synthesized from the reaction of H_2O_2 and Fe^{2+} can also be used as the heterogeneous catalyst of H_2O_2 . Even the COD and color removal at higher Fe^{2+} concentration and lower Fe^{2+} concentration was no difference.

From the Figure 4.23 illustrated that the total iron remaining in the condition with Fe^{2+} concentration 20 mg/l, 50 mg/l, 75 mg/l and 100 mg/l was 100%, 89.6%, 77.0% and 69.0%, respectively. Decreasing total iron remaining in the solution implied that crystallized iron coated onto the surface of carriers. From the results, the condition, high initial Fe^{2+} concentration (100mg/l), the total iron remaining was 69.0% at 100 minutes. It indicated that Fe^{3+} coated onto the surface of carriers via the crystallization about 31.0% of total iron concentration as shown in Figure 4.23f. As the continuous mode, the iron onto the surface of carriers can be used as the heterogeneous catalyst and the amount of iron sludge was also reduced.

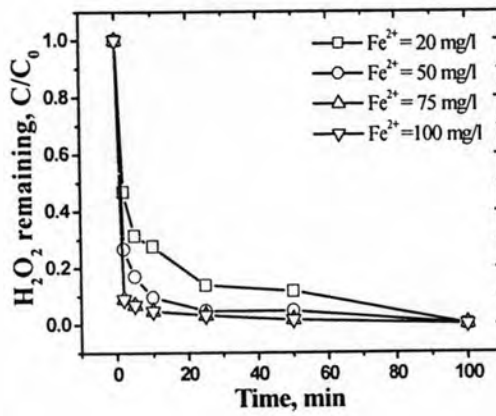
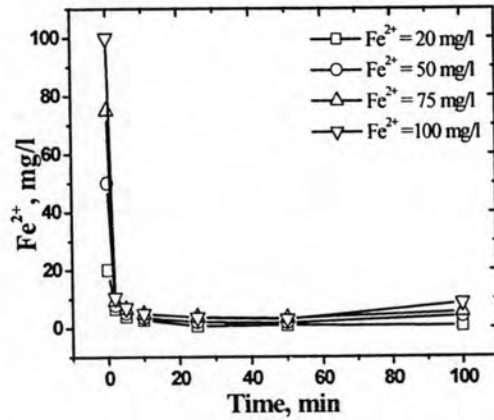
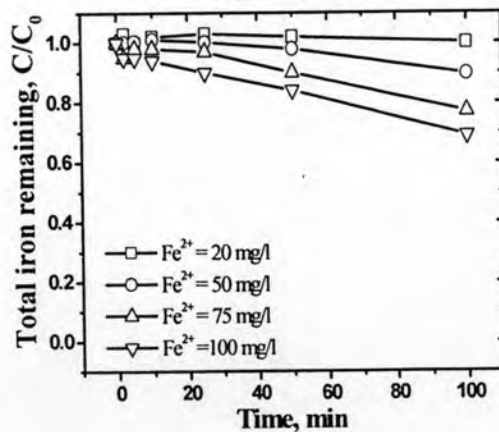
Figure 4.24 shown the comparison of carrier under different Fe^{2+} dosage, the color of carriers under high Fe^{2+} concentration was darker than that under low Fe^{2+} concentration because of iron crystallization.



a) COD remaining



b) Color remaining

c) H₂O₂ remaininge) Fe²⁺ remaining

f) Total iron remaining

Figure 4.23 Effect of Fe²⁺ concentration on COD and color removal of RB5; RB5 = 0.1 mM, H₂O₂ = 160 mg/l, carrier = 74.07 g/l, initial pH = 3 (Appendix J).



Figure 4.24 Comparison of carrier under different Fe^{2+} dosage.
 (*REMARK: 1. Original Carriers, 2. $\text{Fe}^{2+} = 20 \text{ mg/l}$, 3. $\text{Fe}^{2+} = 50 \text{ mg/l}$, 4. $\text{Fe}^{2+} = 75 \text{ mg/l}$, 5. $\text{Fe}^{2+} = 100 \text{ mg/l}$).

4.5 COD and color removals of industrial wastewater

4.5.1 Characteristic of industrial wastewater

This study was performed to investigate the removal of COD and color from a dye manufacturing plant wastewater using the fluidized-bed Fenton process. The industrial wastewater used was collected from Nan-Woei Industrial Co., Ltd that located in Tainan, in South Taiwan. The various waste streams from the dyeing, printing, washing, de-sizing, scouring, mercerizing, and bleaching operations were collected and combined together in the equalization tank. Currently, the produced dye manufacturing wastewater is treated by activated sludge and chemical coagulation. A summary of important influent characteristics is presented in Table 4.9.

Table 4.9 Characteristics of industrial wastewater.

Parameter	Range
pH	9.43 – 9.58
Color (ADMI units)	609 – 975
COD (mg/l)	314 – 404

4.5.2 Effect of Fe^{2+} on the COD and color removal efficiency of industrial wastewater

From the results of COD and color removal of synthetic reactive dyes, the oxidation rates followed the second-order kinetic. But when the fluidized-bed Fenton process was applied with industrial wastewater, the results of kinetic were different. The results were the same as the investigation of oxidation of dichlorvos with hydrogen peroxide using ferrous ion as catalyst (Lu et al., 1999), it was two-stage reaction. Therefore, the two-stage reaction was explained in this part.

As shown in Figure 4.25a, obviously, it was two-stage reaction; the COD and color removal of industrial before 2 minutes was far more rapid than that after 2 minutes. The main reason for the two-stage reaction is that Fe^{2+} reacted very quickly with H_2O_2 to produce large amount of hydroxyl radicals (see Eq. (4-1)). The produced hydroxyl radicals can react rapidly with organic matter, thus in the first stage, the COD and color of industrial wastewater was decomposed quickly; this is referred to as $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ stage. The Fe^{3+} was produced in the first stage can react with H_2O_2 to produce hydroperoxyl radicals ($\text{HO}_2\cdot$) and Fe^{2+} , and the reactions are shown in Eqs. (4-6) and (4-7).

Hydroxyl radicals ($\text{OH}\cdot$) and hydroperoxyl radicals ($\text{HO}_2\cdot$) formed in the reactions are able to continue to dichlorvos. The reaction rate constant ($\text{M}^{-1}\text{s}^{-1}$) of Fe^{2+} reacting with H_2O_2 to produce $\text{OH}\cdot$ is 53 and the reaction-constant of Fe^{3+} reacting with H_2O_2 to form Fe^{2+} is 0.02 (Sun and Pignatello, cited in Lu et al., 1999: 280). Therefore, it can be derived that the former reaction is far more swifter than the latter, resulting in a higher rate of $\text{OH}\cdot$ formation in the first stage reaction than that in second stage reaction. The rate of oxidation in the second stage was slower than that in the first stage, and the second stage will be referred to here as the $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ stage.

The detection of Fe^{2+} in Figure 4.25d also supports the two-stage reaction for the COD and color removal with Fenton's reagent. Under the condition that different amounts of Fe^{2+} were added, most of the Fe^{2+} transformed to Fe^{3+} , which were undetectable after 2 minutes. In order to first stage and second stage reactions separately, the reaction which occurred in the first stage is discussed by the initial rate, and the COD and color removal in the second stage were slightly decreased, therefore, in the second stage is shown by %COD and %color removal efficiency.

The COD of wastewater from textile factory was unsteady. Hence, the concentration of COD and Fenton's reagent of this part was used in ratio of $[\text{COD}]:[\text{Fe}^{2+}]:[\text{H}_2\text{O}_2]$. To justify this argument, the experiments were performed to examine the initial rates of COD removal at time of 2 minutes against $[\text{COD}]:[\text{Fe}^{2+}]:[\text{H}_2\text{O}_2]$ ranging 1:0.32:3.17 to 1:1.59:3.17.

Since Fe^{2+} ions catalyze H_2O_2 to form hydroxyl radicals quite quickly, it seems also advantageous to utilize Fe^{2+} ions as much as possible. However, the hydroxyl radicals may be scavenged by Fe^{2+} ions. Hence, it is not necessarily true that

ever-increasing ferrous ions dosage will result in proportional removal of COD and color from the wastewater.

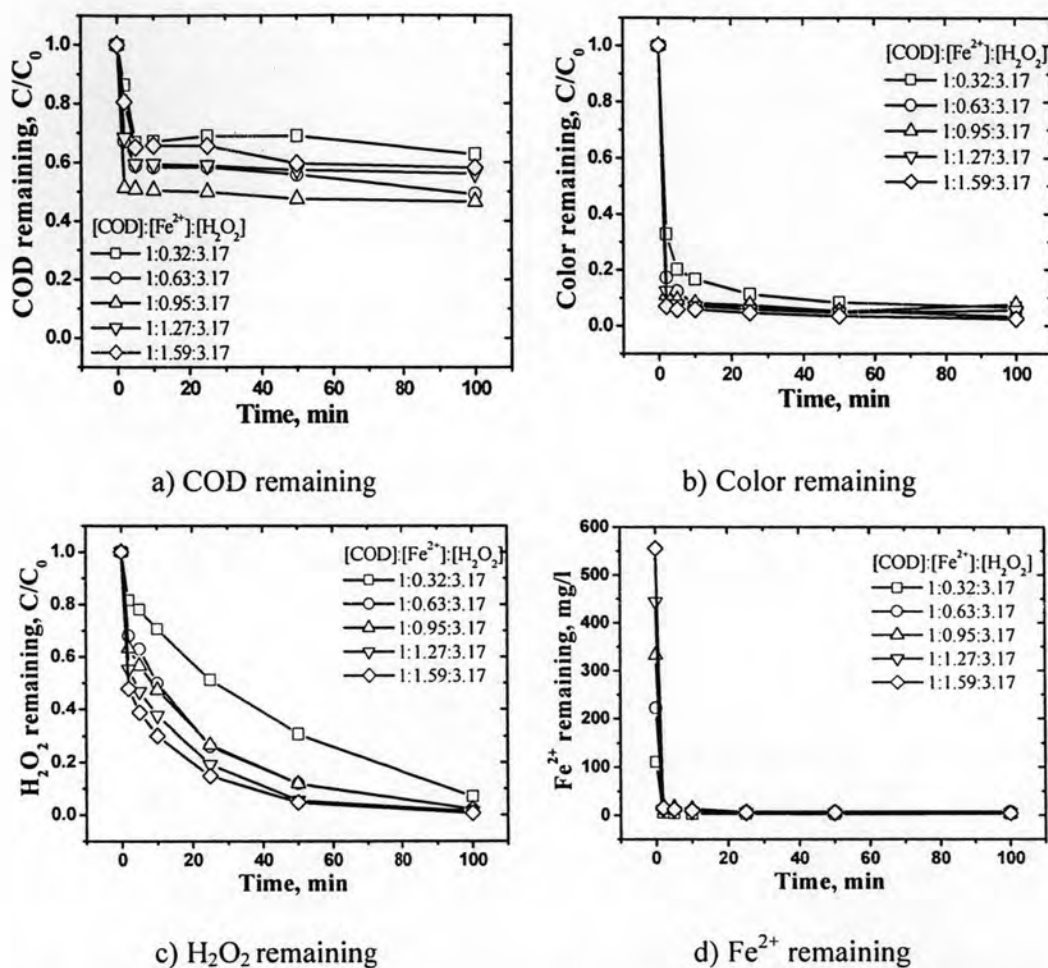


Figure 4.25 Effect of Fe²⁺ concentration on COD and color removal of wastewater from textile factory; [COD]:[Fe²⁺]:[H₂O₂] = 1:0.32:3.17 - 1:1.59:3.17, carrier = 74.07 g/l, initial pH = 3.

Table 4.10 The initial rates of COD removal and %COD removal and %color removal efficiency of wastewater from textile factory under different Fe²⁺ dosage (Appendix K).

[COD]:[Fe ²⁺]:[H ₂ O ₂]	Initial rate x10 ⁻² mg l ⁻¹ min ⁻¹	%COD removal	%Color removal
1 : 0.32 : 3.17	6.8	37.3	93.5
1 : 0.63 : 3.17	16.5	50.9	96.8
1 : 0.95 : 3.17	25.3	55.2	92.5
1 : 1.27 : 3.17	15.8	43.9	94.6
1 : 1.59 : 3.17	9.7	41.8	97.6

As illustrated in Figure 4.25b, the color removal efficiency was higher 92% under any conditions. In comparison, the initial rates of COD removal and %COD removal and %color removal efficiency under different Fe^{2+} dosage were also shown in Table 4.10. It can conclude that when the Fe^{2+} concentration was higher than a specific level, the degradation rate of reactive dyes slightly slows down. The reaction of Fe^{2+} and $\text{OH}\cdot$ in aqueous solution can be expressed by the following Equation (2-7) (Parsons, 2004): $\text{Fe}^{2+} + \text{OH}\cdot \rightarrow \text{OH}^- + \text{Fe}^{3+}$

From the result, the condition $[\text{COD}]:[\text{Fe}^{2+}]:[\text{H}_2\text{O}_2] = 1:0.95:3.17$ is the critical concentration. When a concentration higher than the critical concentration is used, the degradation rate of organic compounds will decrease. Therefore, this study, effect of Fe^{2+} on the COD and color removals efficiency of industrial wastewater, $[\text{COD}]:[\text{Fe}^{2+}]:[\text{H}_2\text{O}_2] = 1:0.95:3.17$ was used in the study of effect of pH on the COD and color removals efficiency of industrial wastewater.

4.5.3 Effect of pH on the COD and color removal efficiency of industrial wastewater

As shown in Figure 4.26 and Table 4.11 illustrated the COD and color removal for fluidized-bed Fenton system as a function of time at which solution pH is systematically varied. The pH of this study focuses on the range of 2.0 – 5.0.

The optimum pH was 3.0, the COD removal and color removal was 53.4% and 92.5%, respectively. And the value of initial rate of COD removal was $24.3 \times 10^{-2} \text{ (mg/l)}^{-1} \text{ min}^{-1}$.

Table 4.11 The initial rates of COD removal and %COD removal and %color removal efficiency of wastewater from textile factory under different pH (Appendix L).

pH	Initial rate $\times 10^{-2}$, $\text{mg l}^{-1} \text{ min}^{-1}$	%COD removal	%Color removal
2	10.3	33.4	89.8
3	24.3	53.4	92.5
4	15.6	37.5	97.9
5	14.6	37.1	88.8

The results were agree with the literature (Hsueh et al., 2005) At pH 2.0 , the COD and color removal efficiency dramatically decreased as shown in Table 4.11, revealing that the scavenging effect of the $\text{OH}\cdot$ by H^+ is severe at low pH. When at a pH higher than 3.0, it also showed low COD and color removal efficiency. It may be explained by the hydrolysis of Fe^{3+} in the solution to reduce $\text{OH}\cdot$ producing rate.

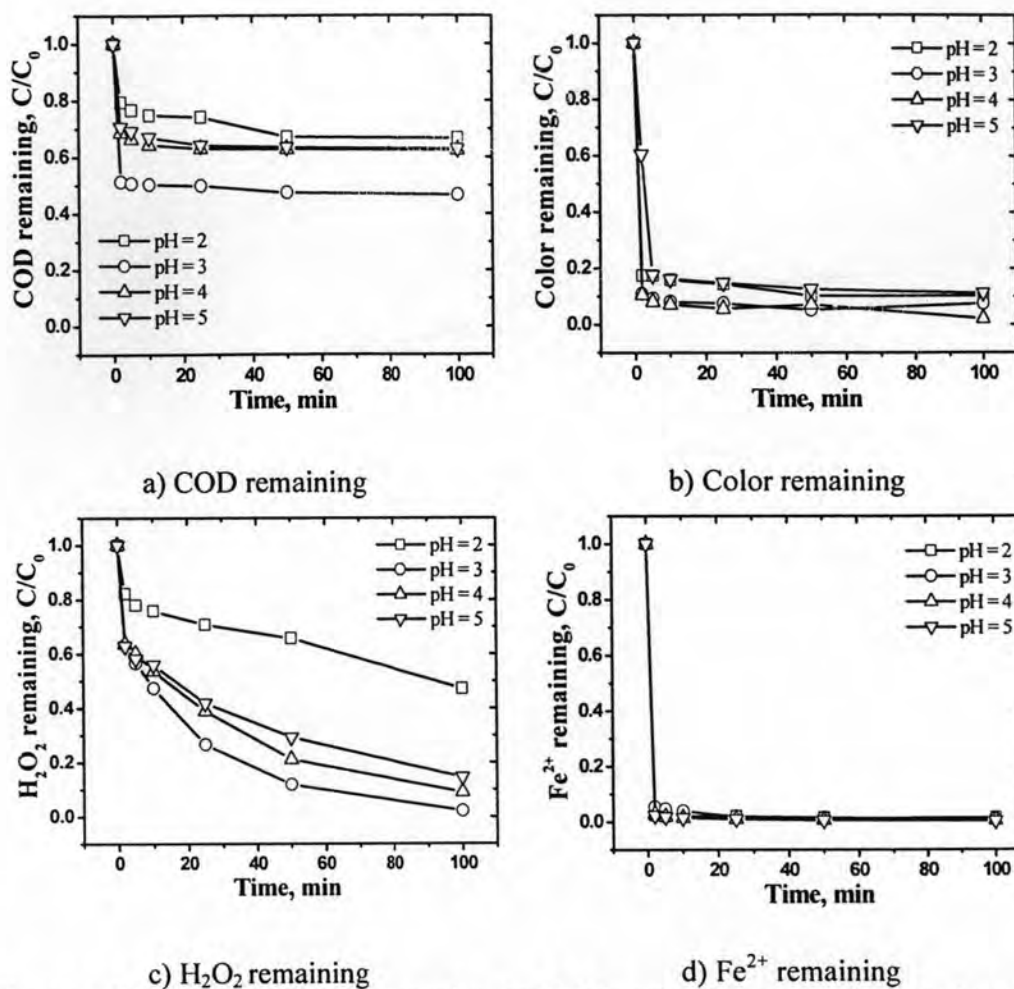


Figure 4.26 Effect of pH concentration on COD and color removal of wastewater from textile factory; $[\text{COD}]:[\text{Fe}^{2+}]:[\text{H}_2\text{O}_2] = 1:0.95:3.17$, carrier = 74.07 g/l, initial pH = 2-5.

4.5.4 Effect of H₂O₂ on the COD and color removal efficiency of industrial wastewater

The reaction rate tends to increase with H₂O₂ concentration. The ratio of H₂O₂ to Fe²⁺ should affect the rate of hydroxyl radical production and scavenging. Hence it is important to use the optimum H₂O₂ and Fe²⁺ concentration.

As shown in Table 4.12 and Figure 4.27, when the ratio of $[\text{COD}]:[\text{Fe}^{2+}]:[\text{H}_2\text{O}_2]$ ranging 1:0.95:3.17 to 1:0.95:7.94 were utilized in the process, the COD and color removal efficiency increased with increasing H₂O₂ concentration. Target remaining COD and color for treating the wastewater from textile factory in this study was less than the discharge standard of Taiwan.

Table 4.12 The initial rates of COD removal and %COD removal and %color removal efficiency of wastewater from textile factory under different H_2O_2 dosage (Appendix M).

[COD]:[Fe ²⁺]:[H ₂ O ₂]	Initial rate x10 ⁻² mg l ⁻¹ min ⁻¹	%COD removal	%Color removal
1 : 0.95 : 3.17	24.3	49.5	92.5
1 : 0.95 : 4.76	25.7	62.2	94.9
1 : 0.95 : 6.35	32.6	71.3	96.5
1 : 0.95 : 7.94	39.4	86.7	96.6

Due to the discharge standards of 1998, textile industries are required by Environmental Protection Administration of Taiwan to comply with the COD and color less than 100 mg/l and 400 in American Dye Manufacturer Institute (ADMI) unit, respectively. (Environmental Protection Administration, ROC., 1998).

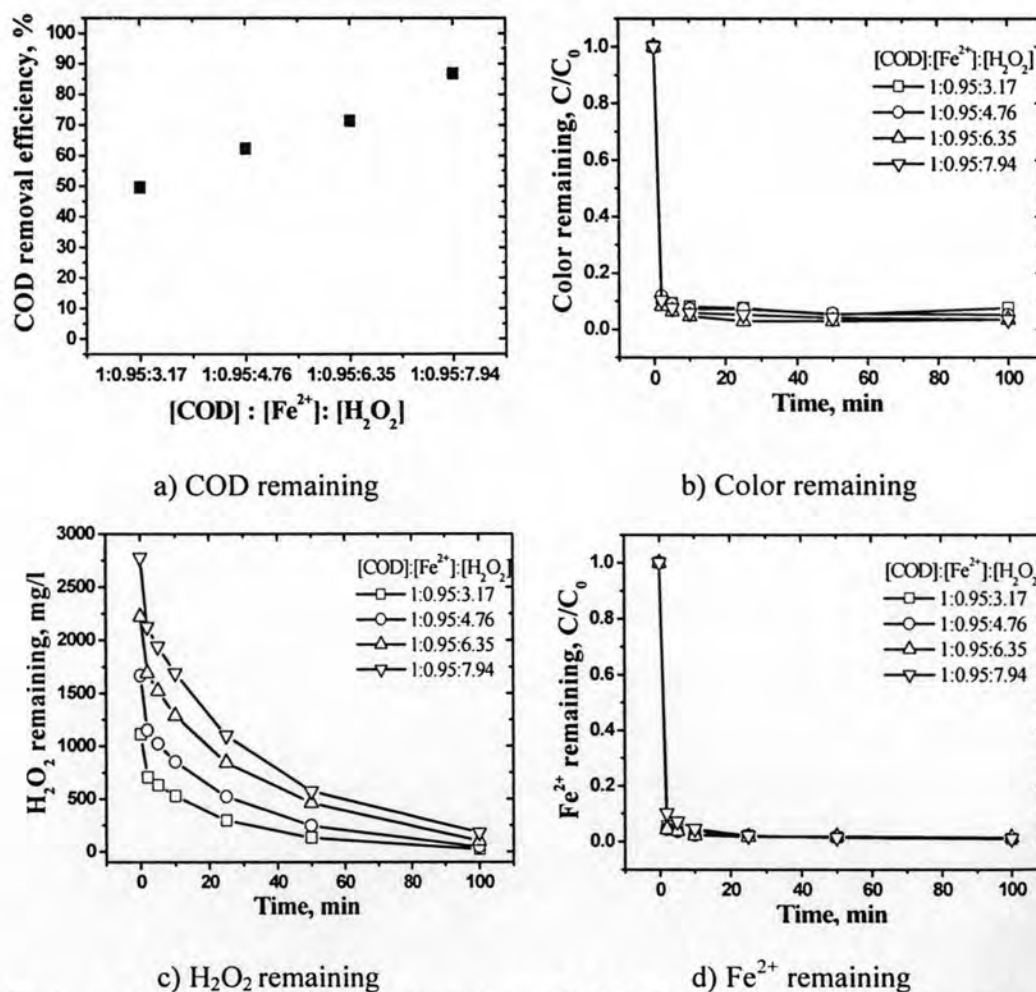


Figure 4.27 Effect of H_2O_2 concentration on COD and color removal of wastewater from textile factory; [COD]:[Fe²⁺]:[H₂O₂] = 1:0.95:3.17 to 1:0.95:7.94, carrier = 74.07 g/l, initial pH = 3.

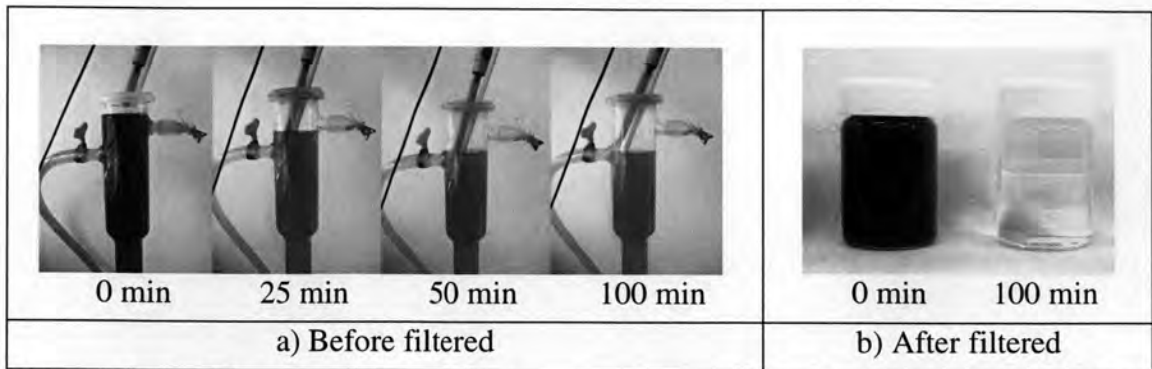


Figure 4.28 Color of industrial wastewater at time interval of 0, 25, 50 and 100 minutes; [COD]:[Fe²⁺]:[H₂O₂] = 1:0.95:7.94, carrier = 74.07 g/l, initial pH = 3.

Figure 4.28 shown that after added Fenton's reagent in the reactor, the color in wastewater was disappeared but the color of Fe(OH)₃ was appeared due to the high dosage of Fe²⁺ concentration. After the sample was filtered, Fe(OH)₃ was removed from the effluent and the sample was clear.

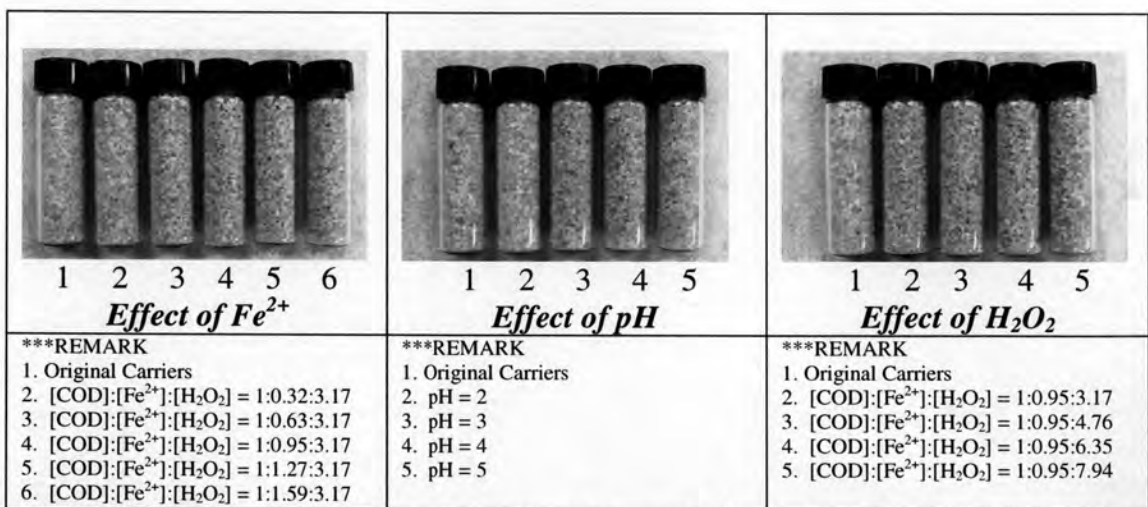


Figure 4.29 Comparison of carrier under different Fe²⁺, H₂O₂ dosage and initial pH for treating the wastewater from textile factory.

From the results, the condition for treating the wastewater of Nan-Woei Industrial Co., Ltd was [COD]:[Fe²⁺]:[H₂O₂] = 1:0.95:7.94, carrier = 74.07 g/l, initial pH = 3 which the effluent COD and color meet the regulatory requirement of Taiwan.