



FBR Technology: Its Potential Application on Reuse of Industrial Wastewater

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Abstract. The treatment performance of the fluidized-bed Fenton process in terms of COD and color removal efficiency on a textile wastewater from a manufacturing facility in Southern Taiwan was evaluated as a case study for the potential application of fluidized-bed reactor (FBR) technology on reuse of industrial wastewater. Results showed that the effluent COD and color of the textile wastewater met the regulatory requirements of Taiwan when the following conditions were used in the treatment: concentration ratio $\text{COD}:\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:0.95:7.94$, carrier = 74.07 g/l, initial pH = 3. The COD and color removal efficiency of the fluidized-bed Fenton process for synthetic commercial dyeing wastewater and actual textile wastewater were compared. At optimum pH = 3, the fluidized-bed Fenton process can remove COD more easily from the commercial dye than from actual textile wastewater. In the case of color removal, the fluidized-bed Fenton had high removal efficiency. This study has shown that the fluidized-bed Fenton process can not only treat textile wastewater to meet Taiwan's regulatory limits for COD and color but also has the potential to be a technology on reuse of industrial wastewater.

Keywords. *fluidized-bed Fenton process, textile wastewater, color removal, industrial water reuse*

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1. Introduction

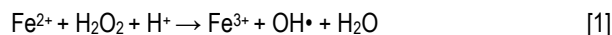
Rapid growth of industries results in corresponding increase in the volume of wastes, solid, or liquid, that will eventually end up polluting the environment if not properly treated before disposal. Treated wastewater can be used for non-potable purposes such as irrigation for agriculture or landscape, cooling water in power plants, or for general cleaning purposes. The reuse of treated water can save on manufacturing costs by providing the additional water requirement of the manufacturing process and thus reduce the use of water from the environment which can be more useful in ecosystems or provide the much-needed water requirement of people.

Many industries are water intensive and the amount of wastewater generated is large. The

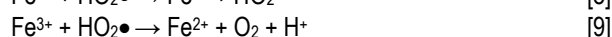
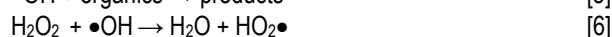
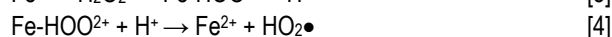
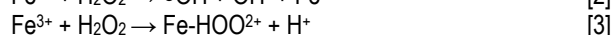
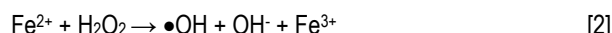
textile industry is one of these. Many of the processes in textile production use aqueous systems and dyes and other chemicals are applied from water baths. The effluents from the textile industry, which are characterized by high values of chemical oxygen demand (COD), total organic carbon (TOC), and strong color, contain soluble and insoluble dyes which when together in one effluent would be difficult to remove or decolorize. Removal of dyes from textile wastewater is very important as many of these are toxic.

Advance oxidation processes have been used in recent years to remove toxic and persistent pollutants (Brillas et al., 2009; El-Desoky et al., 2010; Isarain-Chavez et al., 2011; Kajitvichyanukul et al., 2006; Liou et al., 2004; Saulea and Brillas, 2001). Table 1 shows a comparison of the various advanced treatment technologies of industry wastewater (Chou et al., 2003).

Among various AOPs, Fenton process ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) has effectively treated various organic contaminants. Fenton's reagent is a mixture of H_2O_2 and ferrous ion and applied at acidic pH condition (3–5), which generates hydroxyl radicals according to the reaction,



The use of Fenton processes can lead to the complete mineralization of some organic compounds, converting them to CO_2 , H_2O , and inorganic ions. The following reactions can take place during a Fenton process (Chou et al., 2004; Lu et al., 1999):



However, a major disadvantage of this process is the production of substantial amounts of iron sludge that requires further disposal. This disadvantage can be addressed by using iron oxides in a fluidized-bed reactor as catalysts in oxidizing

the organic contaminants (Al-Hayek and Dore, 1990; Chou and Huang, 1999; Lin, 1997; Valentine and Wang, 1998). In a fluidized-bed Fenton (FBF) process, the amount of precipitation of puffy ferric hydroxide is reduced as the ferric hydrolysis product of Fenton reaction crystallizes and grows on the surface of the carriers (Khunikakorn et al., 2006). Some studies have shown that the fluidized-bed Fenton process had better performance than the conventional Fenton process or other processes based on the Fenton process. Anotai et al. (2010) found that FBF had higher aniline mineralization than electro-Fenton. For organic pollutant and iron removal, FBF can achieve high performance (Boonrattanakij et al., 2011). In another study, FBF had better performance compared with the traditional Fenton process in the removal of 2,4-dichlorophenol (Muangthai et al., 2010). The improved oxidation in the fluidized-bed Fenton that will result in reduction of the formation of sludge is due to the different processes occurring simultaneously: (1) homogeneous chemical oxidation ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$), (2) heterogeneous chemical oxidation ($\text{H}_2\text{O}_2/\text{iron oxide}$), (3) fluidized-bed crystallization, and (4) reductive dissolution of iron oxides.

Table 1

Comparison of various advanced treatment technologies of industry wastewater (Chou et al., 2003).

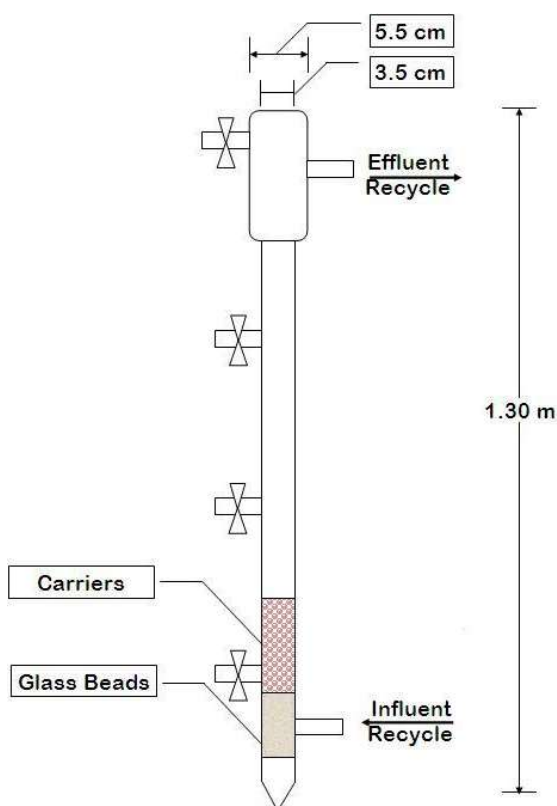
Items	Membrane Separation	Activated Carbon Adsorption	Chemical Coagulation	Ozone Oxidation	Fenton Method	Fluidized-bed Fenton Method
COD removal efficiency (%)	90-95	20-75	20-50	30-60	65-85	70-90
Capital cost (US \$/m ³)	50-1100	260-430	60-140	570-1100	60-140	60-200
Operating cost (US \$/m ³)	0.4-1.0	0.3-1.1	0.1-0.4	0.7-1.0	0.3-0.7	0.25-0.4
Operating cost (US \$/kg COD)	4-10	3-11	1-4	7-10	3-7	2.5-4
Note	Concentration must be treated	Activated carbon must be regenerated	Sludge must be treated	Wasted O ₂ must be treated	Sludge must be treated	Sludge is reduced 70%, compared to Fenton method

* Based on the COD reduction from 200 to 1000 mg/l.

Table 2

Characteristics of synthetic commercial dye wastewater and actual wastewater

Synthetic commercial dye wastewater			Actual wastewater	
Dye	Initial COD (mg/L)	Initial color (ADMI units)	Parameter	Range
Black B	55	6700	pH	9.43- 9.58
Blue ER-A	57	5100	COD (mg/L)	314 – 404
Orange BR2	108	4600	Color (ADMI units)	609 – 975

**Figure 1:** Schematic diagram of the fluidized-bed reactor

In this study, the treatment performance of a fluidized-bed Fenton process in terms of COD and color removal efficiency on a textile wastewater from a manufacturing facility in Southern Taiwan was evaluated as a case study for the potential application of fluidized-bed reactor (FBR) technology on reuse of industrial wastewater. The COD and color removal efficiency of the fluidized-bed Fenton process for synthetic commercial dye wastewater and actual textile wastewater were compared. The performance of the fluidized-bed Fenton process was evaluated for treating actual textile wastewater from a

manufacturing plant in Southern Taiwan to meet Taiwan's regulatory limits on COD and color.

2. Methods

2.1 Materials

Ferrous sulfate Hepta-hydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and 35% Hydrogen Peroxide (H_2O_2) were purchased from Merck. Silica oxide (SiO_2), grain-shaped, with 0.84–2.00 mm particle diameter was used as carrier in the fluidized-bed reactor. The commercial dyes and actual textile wastewater were taken from a manufacturing facility in Southern Taiwan. Table 2 shows the characteristics of commercial dye and actual wastewater from the textile manufacturing facility.

2.2 Fluidized-Bed Reactor

A 1.35-liters fluidized-bed reactor (FBR) was used in all experiments. The reactor is a cylinder consisting of an inlet, outlet, and recirculating section (Figure 1). The silica oxide carrier was fluidized by adjusting the internal circulation at 50% bed expansion (Chou et al., 2004).

2.3 Experimental Procedure

The silica oxide carrier and the textile wastewater were added into the reactor. The recycle pump was turned on to suspend the carrier and mix the solution. The pH was adjusted to 3.0 ± 0.2 (Hsueh et al., 2005) with the addition of H_2SO_4 . Ferrous solution was added. To start the reaction, H_2O_2 was added. At selected time intervals of 0, 2, 5, 10, 25, 50, and 100 minutes, samples were withdrawn from the reactor, injected into tubes containing Na_2HPO_4 to stop the reaction and filtered through 0.45 μm syringe microfilters and then analyzed for residual H_2O_2 , COD, ferrous ion concentration, and color.

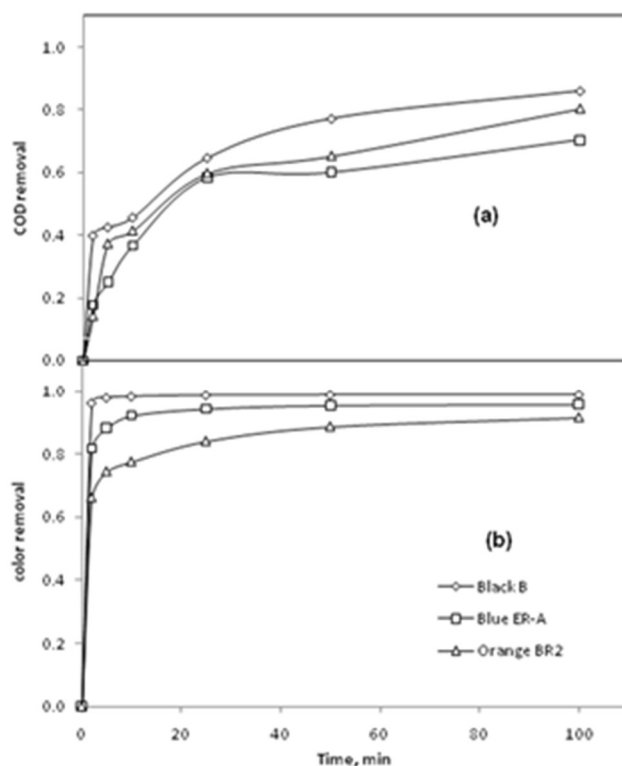


Figure 2: COD and color removal of synthetic commercial dye wastewater; dyes =100 mg/L, Fe^{2+} =20 mg/L, H_2O_2 =160 mg/L, carrier =74.07 g/L and initial pH= 3.

2.4 Analytical Methods

The residual H_2O_2 was determined by standard iodometric method with potassium iodide and $\text{Na}_2\text{S}_2\text{O}_3$ as reactants (Kolthof et al., 1969). The COD was determined using closed reflux titrimetric method (APHA, 1998). The ferrous ion

concentration was determined by measurement of light absorbance at 510 nm using an ultraviolet-visible (UV-Vis) spectrophotometer. The color was analyzed using Colorimetric (ADMI units) standard method.

3. Results and Discussion

3.1 COD and Color Removal of Synthetic Commercial Dye Wastewater

The COD values of the 0.1 mM dyes were very low and color values were very high. It can be seen from Figure 2 and Table 3 that removal of COD and color were high using the fluidized-bed Fenton process.

For the commercial dyes, the COD removal by fluidized bed Fenton process ranged from 70.3–86.1% and color removal ranged from 91.6–98.9%.

3.2 COD and Color Removal of Actual Textile Wastewater

Table 2 shows the characteristics of the actual wastewater from a textile manufacturing facility in Southern Taiwan with COD values at 314–404 mg/L and color at 609–975 ADMI units. These values are much higher than the discharge standards of 1998 by the Environmental Protection Administration of Taiwan which require that the textile industry maintains a COD value of less than 100 mg/L and color of less than 400 American Dye Manufacturer Institute (ADMI) units (EPA ROC, 1998).

Table 3

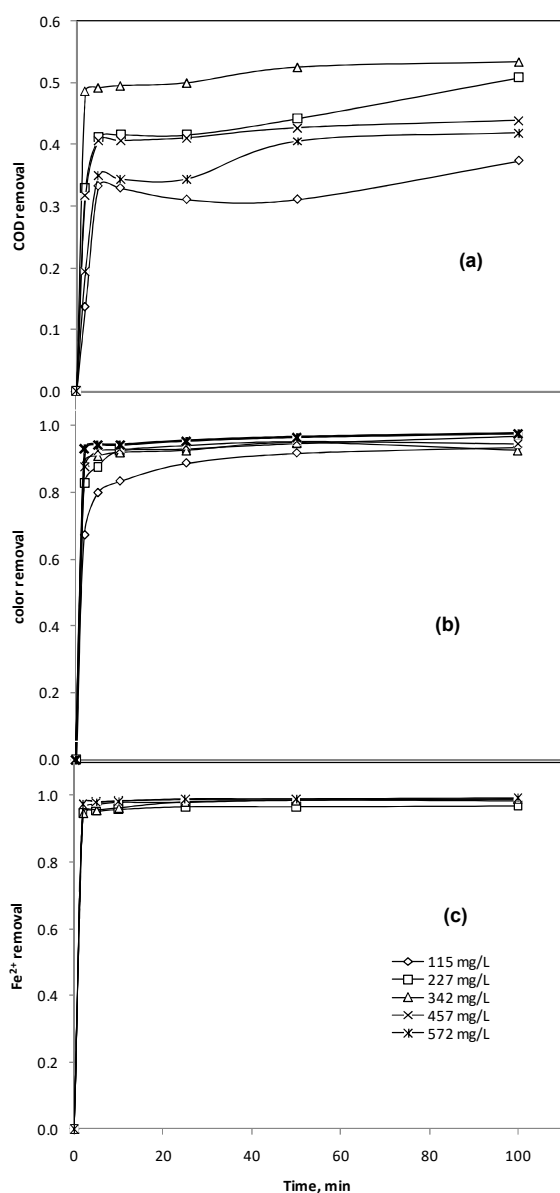
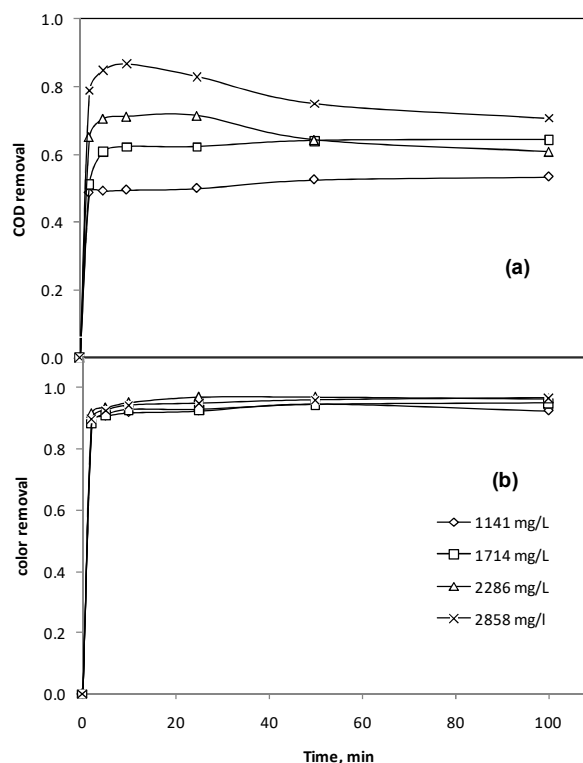
Initial COD and color, % COD and % color removal efficiency of commercial dyes

Dyes	COD Initial COD (mg/l)	Final COD (mg/l)	% COD removal	Color 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

Table 4

Comparison of COD and color after treatment with EPA Taiwan standards

	COD			Color		
	Initial COD (mg/l)	Final COD (mg/l) (86.7% removal)	EPA Taiwan COD standard for textile wastewater	Initial color (ADMI unit)	Final color (ADMI units) (96.6% removal)	EPA Taiwan Color standard for textile wastewater (ADMI unit)
Textile wastewater	314 – 404	42-54	Less than 100 mg/L	609 – 975	207-332	Less than 400

**Figure 3:** Effect of Fe^{2+} on treatment of actual textile wastewater at carrier = 74.07 g SiO_2/L , pH =3, COD: H_2O_2 = 1:3.17**Figure 4:** Effect of H_2O_2 on treatment of actual textile wastewater at carrier = 74.07 g SiO_2/L , pH =3 and concentration ratio COD: Fe^{2+} = 1:0.95

The decomposition of H_2O_2 by the catalytic action of Fe^{2+} to form $\bullet\text{OH}$ (Equation 2) may mean that the more Fe^{2+} are available, the more COD and color are removed from the wastewater. However, this is not the case as Fe^{2+} can scavenge $\bullet\text{OH}$ (Equation 7). The COD value of the actual wastewater was not steady. The optimal dosage of Fe^{2+} necessary to degrade the wastewater was determined using different concentration ratios of COD: Fe^{2+} : H_2O_2 . Figure 3 shows the effect of

Fe^{+2} for the different concentration values in the range of 115 mg/L – 572 mg/L on COD and color removal of the wastewater.

It can be seen in Figure 3(a) that increasing the Fe^{+2} concentration from 115 mg/L to 342 mg/L results in increase in COD removal. However, further increase of Fe^{+2} concentration up to 572 mg/L resulted in decrease of COD removal. The highest COD removal was observed at Fe^{+2} concentration of 342 mg/L. Figure 3(b) shows that increasing the Fe^{+2} concentration increased color removal. It can be further observed that COD and color removal were high in the first 2 minutes of the reaction (Figure 3(a) and 3(b)), and the removal slowed down after 2 minutes until the end of the reaction at 100 minutes. At the end of the reaction at optimum condition of 342 mg/L, the removal efficiency for COD and color were 53.4% and 92.5%, respectively. This showed that the fluidized-bed can easily decolorize textile wastewater than oxidize the organic pollutant present in the wastewater. Figure 3(c) shows that Fe^{+2} was rapidly utilized to catalyze H_2O_2 in the first 2 minutes and that after 2 minutes, Fe^{+2} may be insufficient to react with the available H_2O_2 to produce the $\bullet\text{OH}$ needed to react with the dye thus reducing the COD removal.

Figure 4 shows the effect of H_2O_2 on textile wastewater treatment. It can be seen from Figure 4(a) that COD removal increased when the H_2O_2 increased from 1141 mg/L to 2858 mg/L. Figure 4(b) shows high color removal efficiency of 92.5% to 96.6% when the H_2O_2 concentration was increased from 1141 mg/L to 2858 mg/L. At H_2O_2 concentration of 2858 mg/L, the highest COD removal (86.7%) and color removal (96.6%) were obtained.

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Table 4 shows the comparison of COD and color values after treatment with EPA Taiwan standards. It can be seen that the COD and the color that remained after treatment by the fluidized-bed Fenton process met the regulatory limits of the 1998 discharge standards set by the Environmental Protection Administration for COD and color for textile wastewater (EPA ROC, 1998).

4. Conclusions

At low pH, COD and color removal efficiency dramatically decreased due to the scavenging effect of the $\text{OH}\bullet$ by H^+ . At a high pH, low COD and color removal efficiency were also observed. It may be explained by the hydrolysis of Fe^{3+} in the solution to reduce $\text{OH}\bullet$ producing rate. The optimum pH for industrial wastewater treatment was 3. At optimum pH = 3, it can be seen that the fluidized-bed Fenton process can remove COD more easily from the commercial dye than from actual textile wastewater. In the case of color removal, the fluidized-bed Fenton process had high removal efficiency. The effluent COD and color of the textile wastewater met the regulatory requirements of Taiwan when the following conditions were used in the treatment: concentration ratio $\text{COD}:\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:0.95:7.94$, carrier = 74.07 g/l, initial pH = 3. This study has shown that the fluidized-bed Fenton process can not only treat textile wastewater to meet Taiwan's regulatory limits for COD and color but also has potential to be a technology on reuse of industrial wastewater.

Acknowledgements

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