

Evaluation of predominant reaction mechanisms for the Fenton process in textile dyeing wastewater treatment

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Abstract This research quantitatively evaluated the predominant reactions in a large-scale Fenton process that treated dyeing wastewaters and suggested an economical and effective treatment process. Through plant analysis, it was found that a great part of the COD was removed by ferric coagulation. The comparative evaluation of Fenton oxidation and ferric coagulation revealed that ferric coagulation was the predominant mechanism to remove COD and colour. In Fenton oxidation, the removal efficiencies of SCOD and colour were 67.7% and 84.7%, respectively. In ferric coagulation, those of SCOD and colour were 60.8% and 62.0%, respectively. A combined process with iron coagulation/precipitation and Fenton oxidation reduced the hydrogen peroxide dosage by over 40% compared to a conventional dosage.

Keywords AOP; dyeing wastewater; Fenton process; iron coagulation

Introduction

The wastewater from the textile dyeing industry is characterized by its high temperature, pH, colour and chemical oxygen demand (COD). The COD in dyeing wastewaters contain refractory, toxic and high molecular weight compounds. A dyeing wastewater is, therefore, presumed to be very resistant to microbial degradation. A combined process of biological treatment and chemical oxidation is commonly used in order to meet water quality standards.

The Fenton process, as an advanced oxidation process, is well known for its removal of colour and recalcitrant organics. It is a system based on the generation of very reactive oxidizing free radicals, especially the hydroxyl radical, in acidic conditions (Fenton, 1894; Walling and Kato, 1971). Recently, Fenton oxidation has been applied to the treatment of refractory organics and toxic materials (Gulyas, 1997; Kang *et al.*, 1999), and the removal of colour (Solozhenko *et al.*, 1995; Tang and Chen, 1996). Though the Fenton process has been proved to be effective for recalcitrant wastewater treatment, the predominant removal mechanisms in Fenton processes are not well explained. Kang *et al.* (2002) reported that, in synthetic textile wastewater containing polyvinyl alcohol and a reactive dyestuff, colour and COD respectively were removed mainly by oxidation by the OH radical and Fe³⁺ coagulation. Yoon *et al.* (1998) also reported that the coagulation by iron in the Fenton process had a primary role in the selective removal of organics in a leachate.

The objectives of this research were to quantitatively evaluate the predominant reactions in a large-scale Fenton process that treats 60,000 m³/d of textile dyeing wastewater, and to suggest an economical and effective treatment process for dyeing wastewater that combines coagulation/precipitation and Fenton oxidation.

Methods

Process analysis

This research was conducted using dyeing wastewater after biological treatment at B dye-

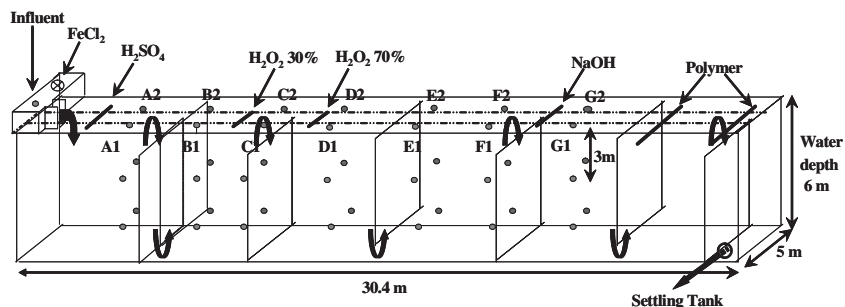


Figure 1 Schematic of Fenton oxidation process at B dyeing wastewater treatment plant and the sampling points (dots)

ing wastewater treatment plant in the Republic of Korea. B dyeing wastewater treatment plant treats 100,000 m³/d produced by 61 dyeing factories. Fenton oxidation is applied to 60% of the total influent and a Fenton-like process is applied for the remaining 40%. The Fenton oxidation process is composed of two parallel channel-type reactors, each of which treats 30,000 m³/d with a hydraulic retention time of approximately 40 minutes.

The schematic of the reactor is shown in Figure 1. The concentration or value of total chemical oxygen demand (TCOD), soluble chemical oxygen demand (SCOD), colour, H₂O₂, Fe²⁺ and pH, were measured in order to elucidate the removal mechanisms of colour and organic matter in the reactor. Colour was measured using the platinum–cobalt method according to Standard Methods (APHA, 1995). The SCOD was analysed as the concentration of the filtrate after filtering by a glass-fiber filter (Whatman, GF/C). The TCOD was measured by taking a sample of a mixture of the liquid and the ferric sludge. H₂O₂ and Fe²⁺ respectively were measured by the peroxide test and the iron test of Reflectoquant® (Merck & Co., Inc.).

Comparison of Fenton oxidation and iron coagulation

Batch-type experiments for Fenton oxidation and ferric coagulation were conducted with 5-L reactors in order to see whether the removal of COD and colour was achieved by oxidation or coagulation in the Fenton oxidation process. Ferrous solution, hydrogen peroxide and other reagents were applied to the Fenton oxidation process by considering the reaction time for each reagent in the treatment plant. Ferric chloride, FeCl₃, was used for coagulation with the same dose as used in the Fenton oxidation. The adjustment of pH was also made throughout the reaction time as observed in the real treatment plant. Aeration was used for mixing as in the plant. The total reaction time was 40 minutes for both experiments of Fenton oxidation and coagulation.

Combined process with iron coagulation and Fenton oxidation

Fenton oxidation after iron coagulation and precipitation of the wastewater was tested because coagulation was effective to remove both organic matter and colour. Coagulation was performed at pH 9 for FeCl₂ and at pH 6 for FeCl₃ for 5 minutes using a jar tester. The iron dose was 150 mg/L for both FeCl₂ and FeCl₃. Fenton oxidation was followed for the supernatant after the iron coagulation and precipitation. The molar ratio of Fe²⁺ versus H₂O₂ for the Fenton oxidation was 1.0. The reaction pH was 3.5 and the reaction time was 30 minutes.

Results and discussion

Process analysis of B dyeing wastewater treatment

Figure 2A shows the concentrations of Fe²⁺ and H₂O₂ at different locations in the Fenton

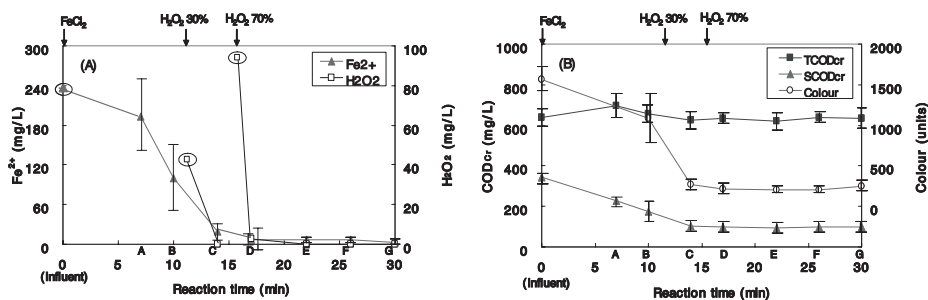


Figure 2 Concentration profiles of (A) H_2O_2 and Fe^{2+} ; and (B) COD and colour for the Fenton process in B treatment plant (○ : injected concentrations of Fe^{2+} and H_2O_2)

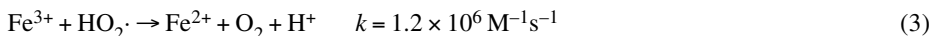
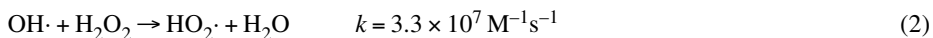
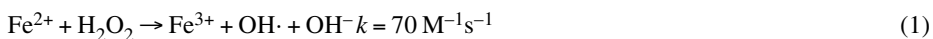
process in B treatment plant. FeCl_2 was injected at the beginning of the reaction, while H_2O_2 was injected at reaction time 12 minutes (30% of total) and 16 minutes (the remaining 70%). The average total doses of hydrogen peroxide and ferrous ion were 135 mg/L and 235 mg/L, respectively. The data shown in Figure 2A are the averages and standard deviations (error bars) of six measurements.

A significant amount of ferrous ion oxidized to ferric ion even before the hydrogen peroxide addition, probably due, partly, to the aeration. On the other hand, hydrogen peroxide degraded quickly and little remained in the samples.

Figure 2B shows the profiles of COD and colour. Each data point also represents the average and standard deviation of six measurements. It is very interesting to note that the concentrations of SCOD began to decrease soon after the ferrous iron injection, that is, before the H_2O_2 injection for Fenton oxidation. However, the TCOD remained almost constant at the initial concentration throughout the reaction time. This indicates that the organic matter was not mineralised by the Fenton reaction, but simply coagulated by the iron. The ferrous solution injected at the beginning of the Fenton process was oxidized rapidly to ferric ion, which caused rapid removal of COD by coagulation. A separate test showed that ferrous ion did not remove SCOD and colour at an acidic pH of 6, a pH that was observed at an early stage of this treatment plant (data not shown). A significant fraction of colour was also removed at the point of B, before H_2O_2 injection. The removal was also achieved by coagulation.

When 30% of the H_2O_2 was injected at reaction time 12 minutes, an additional removal of SCOD was observed. Most of this removal was also caused by coagulation, because the TCOD concentration was little changed. A major fraction of colour was removed after the first injection of H_2O_2 . When the remaining 70% of H_2O_2 was injected at time 16 minutes, only a slight decrease of colour and no decrease of SCOD was observed.

The ratio of $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ was $[0.3 \text{ mM}]/[2.8 \text{ mM}]$ at the moment of 70% H_2O_2 injection. The rapid degradation of H_2O_2 under the shortage of Fe^{2+} was probably due to the chain reactions as shown in reactions (1)~(3) (Yoon *et al.*, 2001). Since the reactions (2) and (3) are so fast, Fe^{2+} can be quickly regenerated from Fe^{3+} , and the regenerated Fe^{2+} consumed H_2O_2 additionally.



Comparison of Fenton oxidation and iron coagulation

The results of Fenton oxidation and coagulation in batch experiments are shown in Figure 3. The patterns of COD and colour removal in the batch Fenton oxidation (Figure 3A) were very similar to those in the wastewater treatment plant (Figure 2B). The TCOD concentration was not changed although a significant reduction of SCOD was observed. The removal efficiencies of SCOD and colour were 71.0% and 84.4% for the treatment plant, and 67.7% and 84.7% for the batch reactor, respectively.

The SCOD in the dyeing wastewater was removed by ferric coagulation (Figure 3B). Again, the TCOD was not changed, providing support that the SCOD removal in the Fenton oxidation in Figures 3A and 2B was by coagulation. A significant removal of colour in this experiment suggested that a certain fraction of colour materials in the dyeing wastewater could be coagulated by ferric ion.

The removal efficiencies of SCOD and colour by ferric coagulation were 60.8% and 62.0%, respectively. These are lower than the efficiencies by Fenton oxidation by 6.9% (SCOD) and 22.7% (colour). From this, we could estimate that at least one quarter of the colour removal and approximately one-tenth of the SCOD removal (not TCOD though) in the Fenton oxidation process was achieved by oxidation. This additional removal of SCOD in the Fenton process was probably achieved by destabilization of organic matter by oxidative radicals.

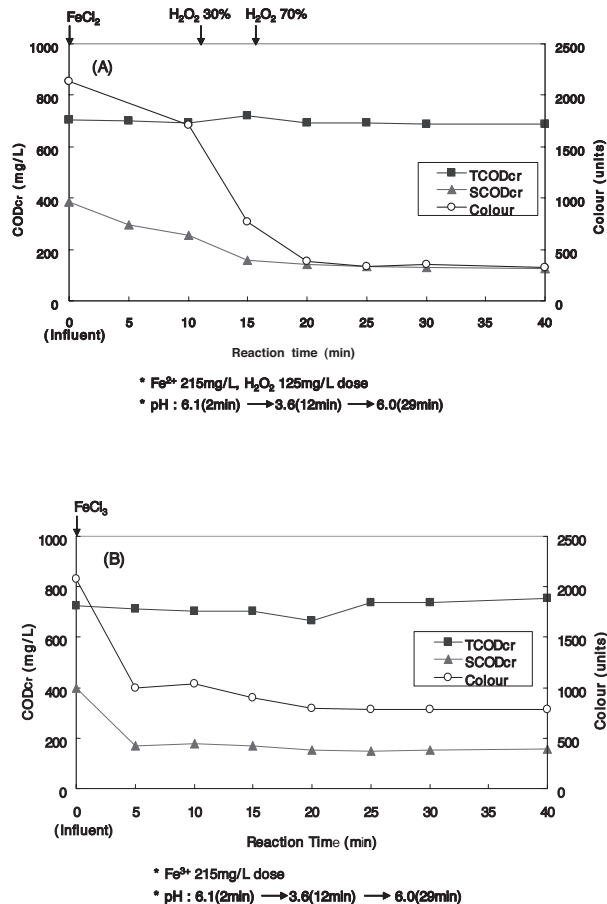


Figure 3 COD and colour changes with (A) Fenton oxidation; and (B) ferric coagulation in batch reactors

Combined process with iron coagulation and Fenton oxidation

Because coagulation was found to be an important mechanism of dyeing wastewater treatment, it was tested to pretreat the wastewater using ferric or ferrous ion before Fenton oxidation in order to obtain process optimisation. First, Fenton oxidation was performed with the supernatant after coagulation with 150 mg/L of ferrous ion. The results are presented in Figure 4. Coagulation with FeCl_2 at pH 9 achieved 40% of SCOD removal and 74% of colour removal. The results of subsequent Fenton oxidation with 2 mM of Fe^{2+} and 2 mM of H_2O_2 for the supernatant were 72% removal of SCOD and 91% removal of colour in total. The removal efficiencies of SCOD and colour using only Fenton oxidation were 68% and 90%, respectively as shown in Figure 4. The sole Fenton oxidation was performed with 224 mg/L of ferrous ion and 135 mg/L of H_2O_2 based on the plant operation conditions.

Fenton oxidation was also performed with the supernatant after coagulation using 150 mg/L of ferric ion. The results are presented in Figure 5. The sole Fenton oxidation was performed with 296 mg/L of ferrous solution and 179 mg/L of H_2O_2 based on the plant operation conditions. In sole Fenton oxidation, removal efficiencies of SCOD and colour were 77% and 93%, respectively. Coagulation with FeCl_3 at pH 6 gave removal efficiencies of 39% for SCOD and 47% for colour. The results of subsequent Fenton oxidation with 3 mM of Fe^{2+} and 3 mM of H_2O_2 for the supernatant were 76% removal of SCOD and 93% removal of colour in total.

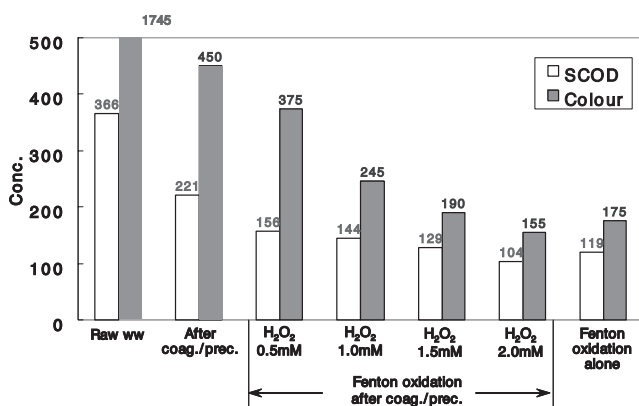


Figure 4 Combined treatment of ferrous (Fe^{2+}) coagulation/precipitation and Fenton oxidation

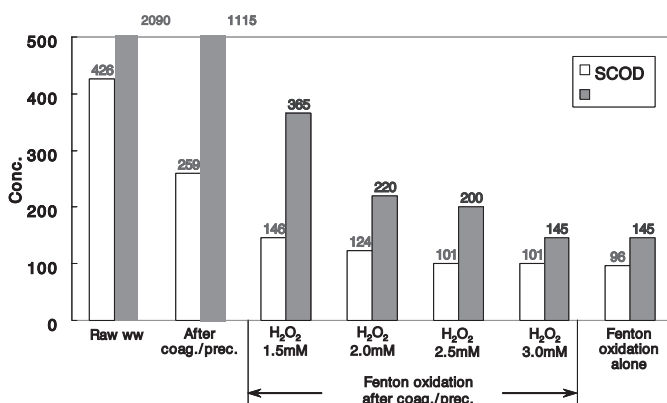


Figure 5 Combined treatment of ferric (Fe^{3+}) coagulation/precipitation and Fenton oxidation

Compared to using only the Fenton oxidation process, for an equivalent removal with a combined process of iron coagulation and Fenton oxidation, a significant saving of H_2O_2 (50% with FeCl_2 coagulation; 43% with FeCl_3 coagulation) was achieved, although slightly more iron was needed. The cost saving by the reduction of H_2O_2 dose was estimated to be as much as 0.5 million US dollar a year for a 60,000 m^3/d treatment.

Conclusions

In the process analysis of B dyeing wastewater treatment, TCOD remained constant at the initial concentration throughout the reaction time in the Fenton oxidation reactor. This demonstrated that the organic matter was not mineralised by the Fenton reaction.

Batch experiments showed that the removal efficiencies of SCOD by Fenton oxidation and ferric coagulation were 67.7% and 60.8%, respectively, and the removal efficiencies of colour by Fenton oxidation and ferric coagulation were 84.7% and 62.1%, respectively. The contributions by pure Fenton oxidation to SCOD and colour removals were about one-tenth (6.9%) and one-quarter (22.7%), respectively, of the total removals. Therefore, the predominant mechanism for the removal of SCOD and colour in B dyeing wastewater was coagulation by ferric ion.

A combined process of iron coagulation/precipitation with subsequent Fenton oxidation was more effective than a sole Fenton oxidation process.

Acknowledgement

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