

Evaluation of Effective Process Operation for the Textile Dyeing Wastewater by Ferrous Solution and Hydrogen Peroxide

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(Manuscript received 2 October, 2004 ; accepted 24 November, 2004)

The purpose of this research is to evaluate the removal efficiencies of COD_{Cr} and color for the dyeing wastewater by the different dosages of ferrous solution and H_2O_2 in Fenton process. In the case of H_2O_2 divided dosage for the Fenton's reagent 7:3 of H_2O_2 was more effective than 3:7 to remove COD_{Cr} and color. The results showed that COD_{Cr} was mainly removed by Fenton coagulation, where the ferric ions are formed in the initial step of Fenton reaction. On the other hand color was removed by Fenton oxidation rather than Fenton coagulation.

The removal mechanism of COD_{Cr} and color was mainly coagulation by ferrous ion, ferric ion and Fenton oxidation. The removal efficiencies were dependent on the ferric ion amount at the beginning of the reaction. However, the final removal efficiency of COD_{Cr} and color was in the order of Fenton oxidation, ferric ion coagulation and ferrous ion coagulation. The reason of the highest removal efficiency by Fenton oxidation can be explained by the chain reactions with ferrous solution, ferric ion and hydrogen peroxide.

Key Words : Fenton oxidation, Coagulation, Removal efficiency, Textile dyeing wastewater treatment

1. Introduction

Many industrial processes using water generate pollutants such as by-products and original compounds, resulting in high pollution loadings to the treatment plant. It has been recognized that hydroxyl radical generated by Fenton's reagent might be tremendously effective work to reduce the intensity of high pollution loads or to remove refractory organic compounds. Other advanced oxidation processes can be applied for the reduction of toxicity and pollution loads. Therefore, they are usually used as pre-treatment to enhance further treatment efficiency¹⁾.

Lau *et al*²⁾ found out that the COD_{Cr} in the UASB effluent was removed by Fenton process, of which 56% was removed by coagulation and precipitation and only 14% by free radical oxidation. It is obvious

that H_2O_2 and Fe^{2+} had a strong synergistic effect on coagulation. Kang *et al*³⁾ have reported that the main removal mechanisms from synthetic textile wastewater containing PVA (polyvinyl alcohol) using Fenton's reagent are Fenton oxidation for color and COD_{Cr} .

Application of Fenton's reagent sequentially as step oxidation rather than one single dose was observed to achieve better oxidation efficiency because of an efficient generation of OH radicals⁴⁾. It was reported that removal efficiencies of pollutant were enhanced by the 2-step dose of Fenton's reagent⁵⁾ and 2-step dose of H_2O_2 ⁶⁾.

This research tries to evaluate the effective process operation and the really effective mechanisms of the Fenton process to remove pollutants for the textile dyeing wastewater. Fenton process as AOP was not exactly evaluated as oxidation and/or coagulation for the highly loaded pollutants. This research was here carried out to evaluate the removal efficiency for the color and COD_{Cr} involving oxidation and/or coagulation and to investigate the mechanisms by comparing the results using ferrous ion, ferric ion and

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Fenton's reagent.

2. Materials and Methods

Fenton's reagent was applied to investigate the exact mechanism to enhance the removal efficiencies of color and COD_{Cr} for the textile dyeing wastewater. A treatment plant with the capacity of 80,000 m³/day for dyeing wastewater is operating, in which the pre-treated dyeing wastewater by biological treatment in the pure oxygen aeration tank without settling tank inflows into the Fenton process. For the evaluation of the removal efficiency total required amount of ferrous solution was applied at once for the initial step. But hydrogen peroxide was applied by divided ratio of 3:7 and 7:3 to compare the removal efficiency and to evaluate the effective dosage method of H₂O₂ as shown in Table 1. The dosing time of H₂O₂ is 5 minute and 11 minute in the case of 3:7 divided dosage of hydrogen peroxide for the sufficient reaction time. In the case of 7:3 divided dose of hydrogen peroxide, the dosing time of H₂O₂ is 5 and 23minutes.

For elucidating the exact mechanisms to remove COD_{Cr} and color three different experiments, that is, Fenton oxidation, ferrous ion coagulation and ferric ion coagulation were performed. The initial COD_{Cr} concentration of wastewater was 380 mg/L. Hydrogen peroxide of 116 mg/L and iron of 197 mg/L were applied to the Fenton process for both experimental conditions. The iron concentration was same for the ferrous coagulation, ferric coagulation and Fenton oxidation. Hydrogen peroxide was applied only to the reactor of Fenton oxidation at 11 minutes and sodium hydroxide was applied at 29 minutes to adjust at pH 5.5 for settling out the ferric sludge.

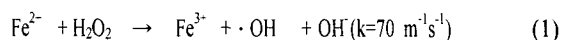
Several items, TCOD_{Cr}, SCOD_{Cr}, Fe²⁺ and H₂O₂ were analysed to evaluate the predominant reaction of Fenton process. TCOD_{Cr} was analysed using the Reactor Digestion Method with COD reactor (Model 45600, HACH) and Direct Reading Spectrophotometer (DR/4000, HACH), SCOD_{Cr} was measured after

filtering through GF/C filter. Color was analysed using ADMI Weighted Ordinate Method with Spectrophotometer (DR/4000, HACH). Analysis of Fenton's reagent, Fe²⁺ and H₂O₂, were carried out using the Reflectometer (Merck, Germany).

3. Results and Discussion

3.1 Effective Dosage H₂O₂ in Fenton Process

Hydroxyl radicals and other radicals as shown in the reaction (1) through (5) are produced by ferrous ion and hydrogen peroxide in Fenton process (Haber *et al.*)⁷⁾. Most of ferrous ion was suddenly converted to ferric ion at the beginning of the reaction.



Total required amount of hydrogen peroxide for Fenton process were separately applied twice, 30% at 5 minutes for the first time and 70% at 11 minutes for the second time of reaction time. The reaction will progress with the excess of ferrous ion at the initial step as shown in equations (1) and (2). Therefore, hydroxyl radicals can be reacted with the excess of ferrous ion instead of reacting with pollutants. On the contrary the competitive reactions for the production of hydroxyl radicals as equations (2) through (5) will randomly happen because hydrogen peroxide is excess in the case of 70% at 5 minutes and 30% at 22 minutes. The ferrous ion concentration at the initial step of Fenton process was rapidly reduced even if hydrogen peroxide did not added as shown in Fig. (1). The hydrogen peroxide was disappeared as soon as the hydrogen peroxide was applied into the reactor as shown in Fig. (1).

Table 1. Dosage of Fenton's reagent and pH conditions in the case of divided dosage of H₂O₂ as

Time(min)	0	5	11	29
Reagent	FeCl ₂ + H ₂ SO ₄	30% of H ₂ O ₂	70% of H ₂ O ₂	NaOH
pH	5.5	3.5	3.5	5.5

The input amount of hydrogen peroxide was disappeared as rapid as at the initial time of reaction. Therefore, ferrous ion for the initial reaction of (1) turns out ferric ion⁸⁾. Ferric ions plays role on coagulation rather than hydroxy radical oxidation to reduce COD_{Cr} and Color. The removal efficiency of COD_{Cr} and Color with ferric ion coagulation showed a little bit lower efficiencies than initial Fenton reaction.

The excess concentration of ferrous ion is not effectively used to reduce color and COD_{Cr} by hydroxyl radicals produced in the case of divided dosage for H₂O₂ as 3:7 and 7:3 because ferrous ions are rapidly converted to ferric ions. The reason for the low removal efficiency of SCOD_{Cr} in the middle of reaction was that residual ferrous ions are not

sufficient to produce hydroxyl radicals before the addition of the H₂O₂ as shown in Fig. 2. Therefore, the effective reaction mechanism can be explained by coagulation rather than oxidation at the beginning of Fenton process. Therefore the first dose of 70% hydrogen peroxide leads the more effective removal of pollutants than the first dose of 30% hydrogen peroxide with total amount of ferrous solution at the beginning of reaction. The ferrous solution with the sufficient amount of hydrogen peroxide was rapidly converted into the ferric ion that was participated in the coagulation.

3.2 Coagulation and Catalytic Oxidation

Three experiments were performed in order to investigate the effective reaction with ferrous ion

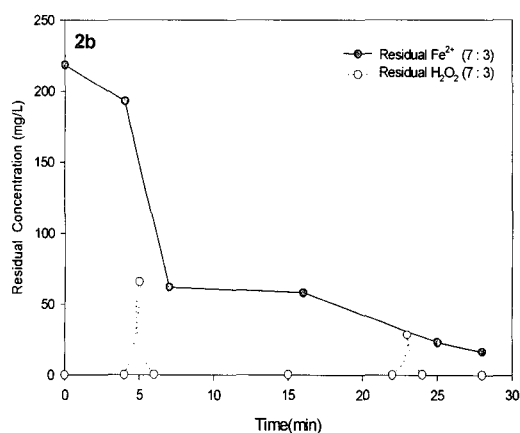
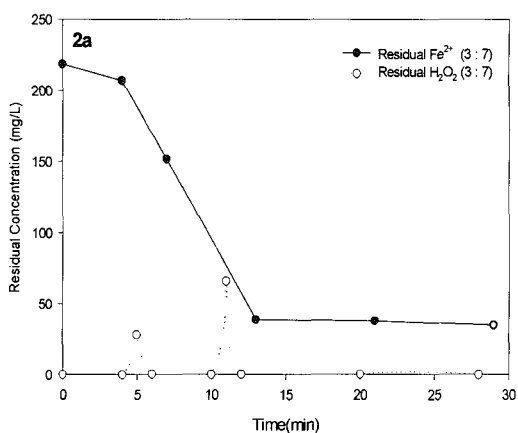


Fig. 1. Residual concentrations of ferrous ion and hydrogen peroxide during the Fenton process. (2a ; 3:7 2b ; 7:3)

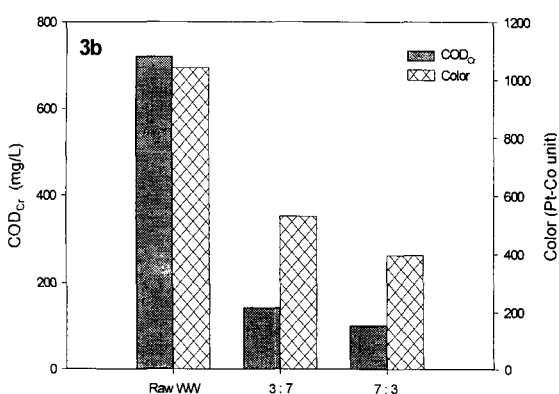
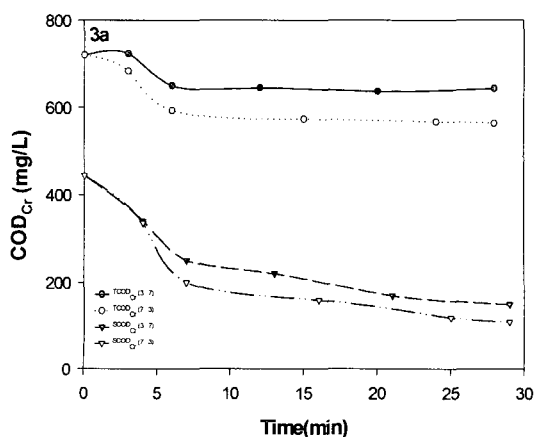


Fig. 2. Concentration profiles of TCOD_{Cr}, SCOD_{Cr} (3a) and the results of color, SCOD_{Cr} (3b) for Fenton process.

coagulation, ferric ion coagulation and Fenton's reagent that are hydrogen peroxide and ferrous solution. These results are presented in Fig. 3. All reactors were adjusted pH at 5.5 same as based on the pH condition of the treatment plant for the initial condition. The concentration of ferrous ion and ferric ion were 200 mg/L for the initial reaction condition. The concentration of hydrogen peroxide of 116 mg/L was only applied to the reactor of Fenton oxidation at the 11 minutes of reaction hour because the application of hydrogen peroxide was same in the textile dyeing wastewater treatment plant. Sodium hydroxide was applied to the all reactors at 29 minutes for the coagulation and sedimentation.

The removal profiles of COD_{Cr} were close to each other for the ferrous coagulation and Fenton oxidation through 12 minutes, however its profile of COD_{Cr} for the ferric coagulation was quite different from them as shown in Fig. (3a). The removal profile of COD_{Cr} with ferric ion was rapidly dropped from the initial step of reaction. However the values of COD_{Cr} by ferric ion coagulation were sustained consistently through the reaction hour after the abrupt drop at the beginning of the reaction.

The ferrous solution was applied to both reactors of the Fenton oxidation and the ferrous coagulation with the same conditions in order to investigate the final difference of COD_{Cr} . The status of ferrous ion was changed to $Fe(OH)_2(s)$ instead of sole ferrous ion by adjusting pH at 5.5. Therefore, the sudden decrease of COD_{Cr} were appeared both the ferrous coagulation and Fenton oxidation even if the removal

efficiency was less than by ferric coagulation. The second drop of COD_{Cr} was appeared after the addition of hydrogen peroxide at 12 minutes maintaining pH 3.5 for Fenton oxidation and another drop of COD_{Cr} was appeared after the addition of NaOH to adjust at pH 5.5 for the sedimentation at 29 minutes of reaction. The decrease amount of COD_{Cr} after sudden drop at 12 minutes in Fenton oxidation exceeded the decrease amount of COD_{Cr} in the ferric coagulation. It can be explained that even if same amount of iron was applied to both reactors a few more decrease of COD_{Cr} after that point was the effect of the additional reactions by equations (3) though (5).

The fate of ferrous ion has been changed ferrous ion to $Fe(OH)_2(s)$ to be used ferrous coagulation at the beginning of reaction. The reaction mechanisms of the removal of COD_{Cr} for the Fenton oxidation can be explained that the rapid decrease of COD_{Cr} before addition of H_2O_2 was the coagulation by $Fe(OH)_2(s)$ rather than by ferric ion.

The rest of ferrous ion encountered with hydrogen peroxide at 12 minutes in the middle of reaction then produced the strong oxidants, OH radicals and ferric ions as presented in equation (1). The kinetic of the reaction is relatively slower than any other reactions, equation (2) through (4). The rest of ferrous ion can react with hydroxyl radical as soon as hydroxyl radical was produced then ferric ion can be produced. The kinetic of the reaction is very fast as shown in equation (2). The ferric ion converted from the most of ferrous ion takes part in coagulation. The rapid

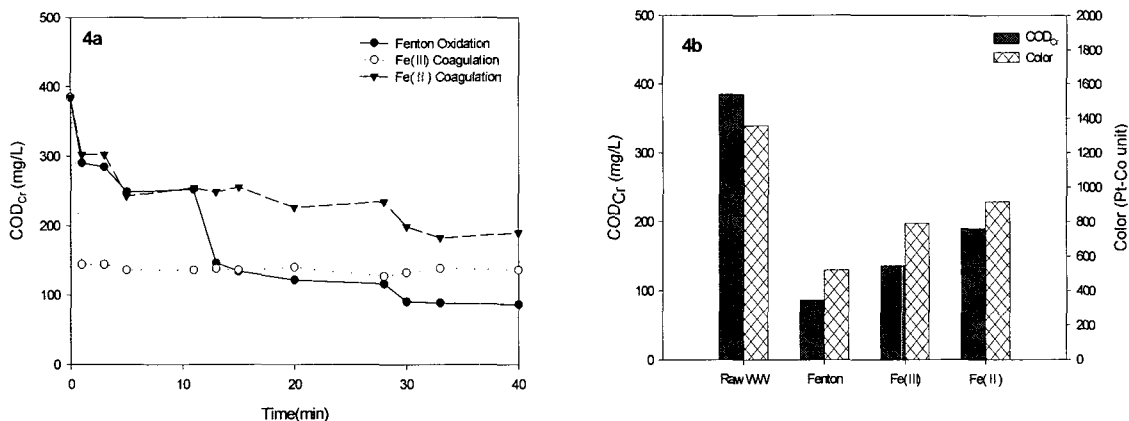


Fig. 3. The COD_{Cr} profile (4a) and final results (4b) for Fenton oxidation, ferrous coagulation and ferric coagulation.

decrease of COD_{Cr} after addition of H_2O_2 will be this mechanism. In addition to the coagulation mechanism oxidation with OH radical will induce the supplemental decrease of COD_{Cr} . The ferric ion, hydroxyl radical and super oxide radical will be produced at the moment of H_2O_2 addition to the reactor as expected reactions of equation (1) through (3). The rest equations (4) and (5) lead to produce ferrous ion from ferric ion. The super oxide radical can be produced by the addition of H_2O_2 with ferric ion and also disappeared by ferric ion. The ferrous ion can be produced by equation (4) and (5) therefore some of hydrogen peroxide might react with this ferrous ion again. Several chain reactions will be happened in the reactor, that is, ferric ion takes part in coagulation and hydroxyl radicals lead oxidation. These results can be explained the difference between the sole ferric ion coagulation and Fenton oxidation.

4. Conclusions

The results of this research indicate that the removal efficiencies of COD_{Cr} and color are strongly dependent on the initial concentration of ferrous solution in Fenton process for textile dyeing wastewater treatment. The optimum condition obtained from this research is that input concentration of hydrogen peroxide can be reduced as much as the residual concentration of the ferrous ion. Coagulation was the predominant reaction for the Fenton process either with the divided dosage of H_2O_2 as 3:7 or 7:3 of the total amount. The higher removal efficiency from Fenton oxidation than from the sole ferric coagulation can be explained by the reason of chain reactions of ferrous solution and hydrogen peroxide. The efficiency of coagulation and oxidation by Fenton oxidation exceeded the efficiency of the sole coagulation by ferric ion to remove COD_{Cr} and color for the textile dyeing wastewater.

Acknowledgements

Authors wish to represent their gratitude for the financial support by Sangmyung University.

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