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EFFECTS OF REACTION CONDITIONS ON THE OXIDATION EFFICIENCY IN THE FENTON PROCESS

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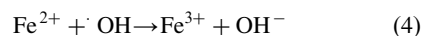
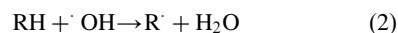
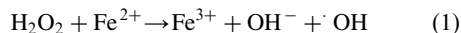
Abstract—The purpose of this study is to efficiently operate Fenton's oxidation process with quantitative analysis of the amount of the organic substances removed by oxidation and coagulation in treatment of the non-biodegradable landfill leachate by Fenton's reagents. The sample used was the biologically treated leachate in the Kimpo metropolitan landfill site in Korea and its COD, BOD₅, NH₃-N and Cl⁻ concentrations were about 1500, 30, 1300 and 4500 mg/l, respectively. The COD removal by oxidation of the organic substances with hydrogen peroxide was most efficient in the pH range of 2.5–4. However, it drastically decreased according to the pH value above 5. The COD removal efficiency by coagulation increased with the increase of the ferrous sulfate dosage, but the overall efficiency over a minimum dosage of 500 mg/l was scarcely changed. The efficiency of hydrogen peroxide actually used in the oxidation of the organic substances was only about 45%. The optimum range of the coagulation pH to maximize the COD removal efficiency by coagulation was 3–6, but that was slightly lower than the pH range of 6–9 generally known in the literature. © 2000 Elsevier Science Ltd. All rights reserved

Key words—Fenton's oxidation, landfill leachate, coagulation, COD removal efficiency, hydrogen peroxide

INTRODUCTION

Landfill leachate is a complicated waste, and it always contains high strength pollutants which have an adverse effect on the environment. The biological treatments including anaerobic and aerobic processes have been shown to be very effective in the early stage because the BOD/COD ratio of the leachate had a high value, but its ratio generally decreased with an increase in the age of landfill (Chian and DeWalle, 1977). Consequently, the biological treatments became ineffective for the treatment of old landfill leachates (Medez *et al.*, 1989). To treat these old or refractory landfill leachates, many physical/chemical and biophysical processes have been used. One available treatment technology of these processes widely used in recent years is Fenton's oxidation process that is possessed of the advantages of both oxidation and coagulation processes (Huh *et al.*, 1996; Lee *et al.*, 1996). In this advanced oxidation process, the organic substances are reacted with hydrogen peroxide in the presence of inexpensive ferrous sulfate to reduce toxicity and COD. More recent research has demonstrated that

the oxidation mechanism by Fenton's reagent was due to the reactive hydroxyl radical generated in an acidic solution by the catalytic decomposition of hydrogen peroxide. Its mechanism (Harber and Weiss, 1934; Barb *et al.*, 1951) is as follows:



As shown in the above reactions, hydrogen peroxide is used for the oxidation of organic substances and ferrous iron. It acts as a reductant when reacting with a strong oxidizing agent such as potassium dichromate, and generates the free oxygen with decomposition by itself. Consequently, the mechanism of these reactions with respect to hydrogen peroxide is very complex and may change with conditions of the reaction and the type of catalyst (Snell and Ettore, 1971). Generally, Fenton's oxidation process was composed of four stages (Bigda, 1995), which are: pH adjustment, oxidation reac-

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tion, neutralization and coagulation, and precipitation. So, the organic substances are removed at two stages of the oxidation and the coagulation. In the literature (Oh *et al.*, 1994), the overall COD removal efficiency of Fenton's oxidation process has been investigated. Lee *et al.* (1996) mentioned that the COD removal efficiency by coagulation with formation of the ferric hydroxo complexes is higher than that by oxidation reacted with hydrogen peroxide. However, the quantitative study of the effect of the operating conditions on the oxidation efficiency of hydrogen peroxide has not yet been reported in the literature. In this study, the effects of several process conditions such as pH, dosage of hydrogen peroxide and ferrous sulfate on the COD removal efficiency were investigated, and the efficiency of hydrogen peroxide actually used to oxidize the organic substances was measured.

MATERIALS AND METHODS

The leachate used, which had been biologically treated by two processes, anaerobic and aerobic, was obtained from Kimpo metropolitan landfill in Korea and stored at 4°C until use. Its characteristics were pH 8.7, COD 1200–1500 mg/l, BOD₅ 30 mg/l, NH₃-N 1300 mg/l, Cl⁻ 4500 mg/l, NO₂-N 350 mg/l, NO₃-N 300 mg/l, and alkalinity as CaCO₃ 5900 mg/l.

A 2 l beaker equipped with a glass bar of 10 mm diameter as a baffle was used as a reactor for this study and the reaction was conducted in an isothermal water bath controlled with 25 ± 1°C. The leachate was mixed with a magnetic stirrer. The reactor was first filled with 1 l of leachate and the pH was adjusted with concentrated sulfuric acid. The second step was the addition of ferrous sulfate (analytical grade, heptahydrate) dissolved in 5 ml of distilled water. The third step was the addition of hydrogen peroxide (reagent grade, 30%) and the reaction was started when the unreacted hydrogen peroxide was not present in the reactor. The concentration of hydrogen peroxide was measured using the iodometric method (Jeffery *et al.*, 1989). Normally, the reaction was finished within about 3 h. The pH was controlled with an accuracy of ±0.02 by adding either sodium hydroxide or sulfuric acid during the reaction period. After the reaction was finished, the COD value of the treated leachate was measured, and its pH adjusted if necessary. It was moved to a graduated cylinder, and was allowed to precipitate until the volume percent of the precipitate was lower than 20%. After the precipitation was complete, the upper liquid of 80% was separated from the precipitate, and then the COD values of the two separated samples were measured.

All the COD values were measured by the closed reflux colorimetric method (APHA, 1995) with a UV-visible spectrophotometer (Shimadzu Co., Model UV-2100). To remove the interference of nitrite when this analysis method is used, sulfamic acid should be added to the dichromate solution. Because sulfamic acid was not added to its solution in the COD analysis, the measured COD values include the oxygen demand used to oxidize nitrite to nitrate as well. Thus, to consider the effect of the nitrite ion on the COD values, the concentrations of nitrite and nitrate were separately measured by ion chromatography (Shimadzu Co., Model LC-10AD).

RESULTS AND DISCUSSION

Figure 1 shows the effect of the pH reaction on the COD removal efficiency in Fenton's oxidation. These results were obtained from the COD values of the upper liquid and the precipitate after the precipitation of the pH reaction without pH adjustment. The COD removal efficiency by oxidation is rarely influenced by pH below the reaction of pH 4; however, it was rapidly decreased with increasing pH reaction in the range of 4–7. In the above reaction of pH 7, COD removal by oxidation scarcely occurred. Hydrogen peroxide was most stable in the range of pH 3–4, but the decomposition rate was rapidly increased with increasing pH above 5 (Meeker, 1965). In a pH reaction higher than 5, the COD removal efficiency by oxidation was rapidly decreased, not only by decomposition of hydrogen peroxide (Feurstein *et al.*, 1981), but also by deactivation of a ferrous catalyst with the formation of ferric hydroxo complexes (Bigda, 1995). The coagulation scarcely occurred in pH 2 and it more easily occurred with increasing pH. However, as shown in Fig. 1, the optimum pH range for COD removal by coagulation was 3–6. The overall COD removal efficiency was shown to be maximum around a reaction of pH 3.5, and it rapidly decreased with increasing pH above 6 because COD removal by both the oxidation and coagulation was decreased with increasing pH.

Figure 2 shows the effect of the ferrous sulfate dosage on the COD removal efficiency. The COD removal efficiency by coagulation was increased by increasing the ferrous sulfate dosage, but the COD removal efficiency by oxidation slightly decreased. These results were in accord with that proposed by Merz and Waters (1949) and Walling and Kato (1971), which better maintained the lower value of the ratio of the catalyst to the concentration of the

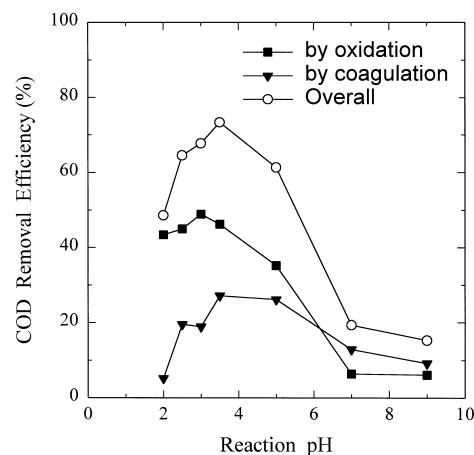


Fig. 1. Effect of the pH reaction on the COD removal efficiency by oxidation and coagulation in Fenton's oxidation (reaction conditions: H₂O₂ = 1650 mg/l; FeSO₄ = 1750 mg/l; temperature = 25°C).

organic substances. The minimum amount of hydrogen peroxide used to oxidize the ferrous sulfate was 2000 mg/l to 223 mg/l; this quantity could not be ignored in comparison to the dosage of hydrogen peroxide used in this study. The overall COD removal efficiency over the dosage of ferrous sulfate of 500 mg/l scarcely changed, but it decreased after decreasing the dosage of ferrous sulfate to less than 500 mg/l because of the rapid reduction of the COD removal efficiency by coagulation. It was shown to be similar to the results of Oh *et al.* (1994), but they indicated that the dosage of ferrous sulfate had a great effect on the reaction time. Since the overall COD removal efficiency scarcely changed after decreasing the dosage of ferrous sulfate over 500 mg/l, it gives merit to the cost reduction and the increase of the COD removal efficiency by oxidation. However, the initial investment cost increases according to the increasing reaction time, and, therefore, the optimum dosage of ferrous sulfate should be determined by considering these two adverse factors.

Figures 3 and 4 show the effects of the dosage of hydrogen peroxide and ferrous sulfate on the COD removal efficiency. Both the overall COD removal efficiency and the efficiency by oxidation in Fig. 3 were increased by increasing the dosage of hydrogen peroxide. As it appeared in the intercept of the y-axis of Fig. 4, in which hydrogen peroxide was not added, the removed COD value by oxidation was about 380 mg/l. These results were obtained by using 350 mg/l of nitrite, which was removed by adjusting the pH to 3.5 and by the addition of ferrous sulfate. Jun *et al.* (1996) showed that the nitrite ion could be readily oxidized by oxygen with ferric and/or ferrous ion, as a catalyst in the acidified solution. Consequently, it was due to the COD analysis using the dichromate solution without the

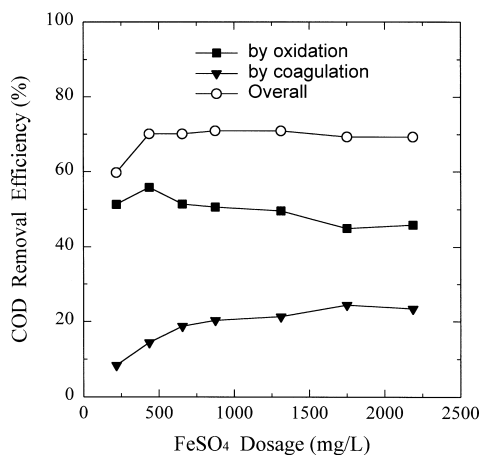


Fig. 2. Effect of the ferrous sulfate dosage on the COD removal efficiency by oxidation and coagulation in Fenton's oxidation (reaction conditions: $\text{H}_2\text{O}_2 = 1650$ mg/l; pH reaction = 3.5; temperature = 25°C).

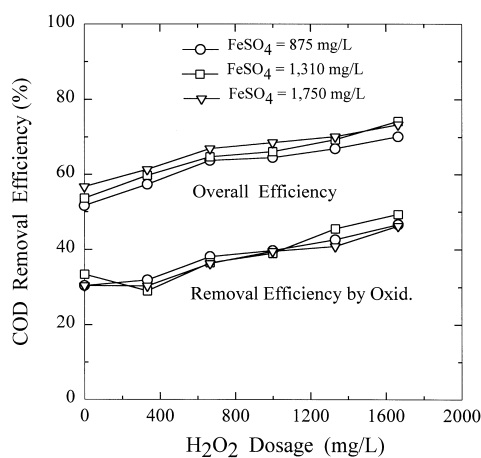


Fig. 3. Effect of the hydrogen peroxide dosage on the COD removal efficiency by oxidation and coagulation in Fenton's oxidation (reaction conditions: pH reaction = 3.5; temperature = 25°C).

addition of sulfamic acid that is used to eliminate the effect of the interference of nitrite on the COD value. As shown in Fig. 1, the removed COD value by oxidation above a pH reaction of 7 was only about 100 mg/l. Its COD value had shown lower than that of the effect of nitrite on the COD value. Because the oxidation rate of the nitrite ion was scarcely affected by pH (Jun *et al.*, 1996), the nitrite ion was perfectly oxidized to the nitrate ion by hydrogen peroxide which is a more powerful oxidant than oxygen. Therefore, it was estimated that since the reaction was not completely terminated, residual hydrogen peroxide had an effect on the measured COD values (Kang *et al.*, 1999). Also, the COD removal efficiencies by oxidation and coagulation at a pH of 3.5 have a maximum efficiency

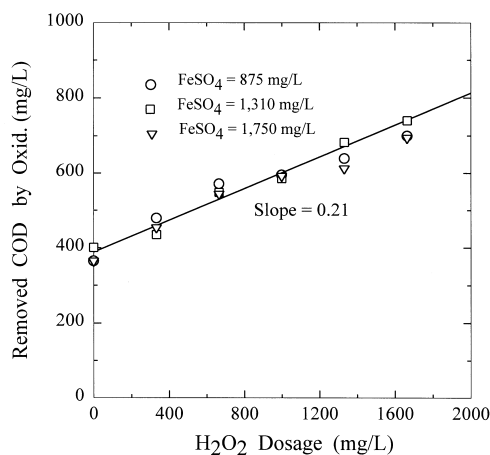


Fig. 4. Plot of the removed COD by oxidation against the hydrogen peroxide dosage in Fenton's oxidation (reaction conditions: pH reaction = 3.5; temperature = 25°C).

except for the effect of nitrite on the COD values which were 38 and 34%, respectively.

The theoretically removable COD value of hydrogen peroxide, 1000 mg/l was 470.6 mg/l, and thus the efficiency of hydrogen peroxide, η , is defined as follows:

$$\eta(\%) = \frac{\text{COD}_{\text{oxid}}}{0.4706 \times [\text{H}_2\text{O}_2]} \times 100 \quad (5)$$

where COD_{oxid} is the removed COD value by oxidation and $[\text{H}_2\text{O}_2]$ is the dosage of hydrogen peroxide. Figure 4 shows the slope in which the plot of the removed COD values by oxidation versus the dosage of hydrogen peroxide was 0.21. Consequently, the efficiency of hydrogen peroxide according to the above definition was about 45%. Though the effect of the dosage of hydrogen peroxide on its efficiency could not be obtained from these experimental results, it can be estimated that the efficiency of hydrogen peroxide by increasing the dosage over a reasonable amount is gradually decreased because the fraction of the organic substances, which cannot be oxidized, is increased. In the literature (Oh *et al.*, 1994; Huh *et al.*, 1996), the COD removal efficiency was too high compared to the dosage of hydrogen peroxide. It was estimated that the organic substances were removed by coagulation.

Figure 5 represents the experimental results to obtain the optimum coagulation pH. The pH using either concentrated hydrogen sulfate or 20 N sodium hydroxide after the reaction is adjusted, and then precipitated. As shown in the COD removal efficiency by coagulation at the condition of the reaction pH 2.0, its efficiency at the coagulation pH 2.0 was about 5% and was increased by increasing the coagulation pH in the range of 2.0–5.0. In the range of the coagulation pH 5.0–9.0, its effi-

ciency was, on the contrary, decreased by increasing the coagulation pH. The maximum COD removal efficiency by coagulation at the pH reaction of 2.0 was about 25%. The reasonable range of the coagulation pH in order to maximize the overall COD removal efficiency was 3–6.

CONCLUSIONS

From the experiments in treatment of the non-biodegradable landfill leachate by Fenton's oxidation, the following conclusions can be drawn:

1. The COD removal efficiency by oxidation was greatly affected by the pH reaction. The most effective reaction was observed below pH 4.0, but the optimal coagulation pH range to maximize the COD removal efficiency is between 3 and 6.
2. The dosage of ferrous sulfate over 500 mg/l does not increase the overall COD removal efficiency. The optimum dosage of ferrous sulfate should be determined by considering the capital and operating costs.
3. The efficiency of hydrogen peroxide obtained from the removed COD values by oxidation was observed to be about 45%.

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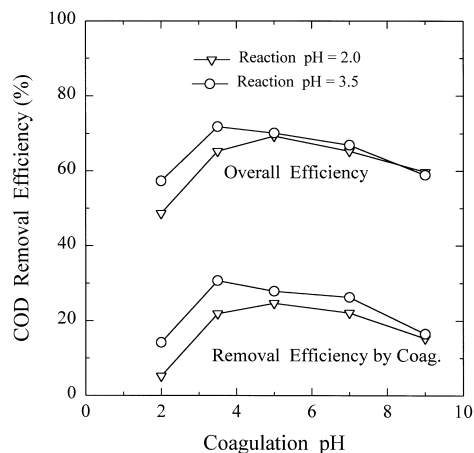


Fig. 5. Effect of the coagulation pH on the COD removal efficiency by coagulation (reaction conditions: $\text{H}_2\text{O}_2 = 1650$ mg/l; $\text{FeSO}_4 = 1750$ mg/l; temperature = 25°C).

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