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The Effect and its Influence Factors of the Fenton Process on the Old Landfill Leachate

Long Tengrui, Anas Al-Harbawi, Zhai Jun and Lin Ming Bo
Faculty of Urban Construction and Environmental Engineering, Chongqing University, 400045, China

Abstract: An experiment study on landfill leachate treatment using Fenton's reagents has been introduced. The effect of operating conditions such as reaction time, pH, H_2O_2 to Fe(II) ratio (W/W) and temperature on the efficacy of Fenton process was investigated. The monitored sample taken from the Chang Sheng bridge landfill site in Chongqing city-China, has its concentrations of COD, BOD_5 and NH_3-N about 1500, 75 and 920 mg L^{-1}, respectively. The oxidation of organic materials in the leachate is pH dependent and the optimal pH is 3.0. The favorable H_2O_2:Fe(II) ratio is 2.5:1 and the COD removal rate increased with the increase of Fenton dosage at the favorable H_2O_2:Fe(II) ratio.

Key words: Fenton process, landfill leachate, biodegradability

INTRODUCTION

The landfill leachate is one kind of wastewater with high concentration of organic compounds, in-organic compounds and sometimes non-trivial level of toxic contaminants such as arsenic and chlorinated organic. The Chemical Oxygen Demand (COD) concentration of typical young leachate can be 36 times as high as the raw domestic wastewater, whereas a mature leachate may be equal in COD concentration to raw sewage, but has much more refractory organic constituents than domestic sewage. Untreated leachate can permeate ground water or be mixed with surface water and contribute to the pollution of soil. Additionally, landfill leachate may cause malodors and aerosols though these effects tend to be temporary and local (Florida Center, 2006; Lin and Chang, 2000). There are many factors affecting the quality and quantity of such leachates, i.e., seasonal weather variation, landfilling techniques, piling and compaction methods, the type and composition of solid waste, structure of the landfill, etc. Above all, the composition of landfill leachates varies greatly depending on the age of the landfill (Lopez *et al*., 2004).

The biological treatment technologies, including anaerobic and aerobic processes, have been shown to be effective in treating the early stage landfill lactates, which has a high BOD/COD ratio. However, this ratio generally decreases with the increase of the age of landfill. Consequently, the biological technologies may become ineffective for treating old landfill leachates. To treat old or refractory landfill leachate, many physical/chemical and biophysical processes have been used. Fenton oxidation process is possessed of the advantages of both oxidation and coagulation. Some recent research had 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 (Lopes de Morais and Zamora, 2005; Kang and Hwang, 2000).

In Fenton process, iron and hydrogen peroxide are two major chemicals determining operation costs as well as efficacy. To understand better and improve the Fenton process (Zhang, 2005). The Fenton reaction has a short reaction time among all advanced oxidation processes and it has other important advantages. Iron and H_2O_2 are cheap and non-toxic, there is no mass transfer limitations due to its homogenous catalytic nature, there is no energy involved as catalyst and the process is easily to run and control. It has been widely used for treatment of highly polluted textile and paper mill wastewaters, as well as pharmaceutical wastewaters (Gotvajn and Končan, 2005). Fenton's reaction is one of the most effective methods of oxidation of organic pollutants that are oxidatively degraded by hydroxyl radicals generated from H_2O_2 in the presence of Fe^{2+} as a catalyst: (Barbusińskil and Filipe, 2001).

$$Fe^{2+}+H_2O_2 \rightarrow Fe^{3+}+OH+OH^- \quad (1)$$

When ferrous salts are used, the hydroxyl radical is produced immediately by the rapid reaction between ferrous ion and hydrogen peroxide (Eq. 1). With ferric

Corresponding Author: Long Tengrui, Faculty of Urban Construction and Environmental Engineering, Chongqing University, 400045, China

salts, the hydroxyl radical is produced in a two-stage process with the slow reaction between ferric ion and hydrogen peroxide (Eq. 2) followed by the rapid reaction between the produced ferrous ion and additional hydrogen peroxide (Barbusińskil and Filipe, 2001; Gotvajn and Končan, 2005):

$$Fe^{3+}+H_2O_2 \rightarrow Fe^{2+}+HO_2^{-}+H^{+} \quad (2)$$

Fenton reaction can be divided into two processes. The first process is an initial oxidation at low pH of about 3. The second process which follows the oxidation process is coagulation at high pH of (7-8). (Yoon *et al*., 1998).

An experiment study on the landfill leachate treatment with Fenton's Reagent has been implemented in Chongqing University to show the influence on the treatment effect caused by several different factors. The experiment results will be introduced and analyzed in this study.

MATERIALS AND METHODS

The leachate investigated in this experiment was taken from The ChangSheng Bridge Landfill inside Chongqing city. The composition can be showed in Table 1. From Table 1, the landfill leachate is characterized as low C/N ratio, low BOD_5/COD ratio and high contents of NH_4-N (1100 mg L^{-1}), which show the leachate can be classified as old and non-biodegradable.

Fenton treatment procedure: Fenton treatment of landfill leachate was carried out at ambient temperature in the following sequential steps: (1) Leachate sample was put in a beaker and stirred by mixing machine. Its pH was adjusted to fixed values by H_2SO_4 98% (w/w). (2) The scheduled Fe^{2+} dosage was achieved by adding the necessary amount of solid FeSO4•7H_2O. (3) A known volume of 35% (w/w) H_2O_2 solution was added in a single step. (4) After fixed reaction time, before carrying out COD tests, adjust pH value to pH 8.0 to remove residual Fe^{2+}(Fe^{3+}). (5) Settle for 30 min and then examine the COD.

Table 1: The Composition of the investigated landfill leachate

Parameter	Unit	Value
COD	mg L^{-1}	1500~2500
BOD_5	mg L^{-1}	50~100
NH_4-N	mg L^{-1}	1100
TN	mg L^{-1}	1300~1400
PO_4-P	mg L^{-1}	12
SS	mg L^{-1}	100
pH		8~9

RESULTS AND DISCUSSION

In this study, we evaluated the efficacy of Fenton process in terms of COD to study the effect of pH, reaction time, Fenton reagent and temperature. COD test is based on the assumption that all the organic materials can be oxidized by the strong oxidizing agent under acidic conditions. Table 2 shows the optimum results in our study to getting the better COD.

Effect of pH value: The pH value can dramatically affect the reaction of oxidation and coagulation in Fenton process. The experiment was conducted under the conditions of Reaction time = 1h, H_2O_2/Fe^{2+} = 1:1 and different pH-values. Figure 1 shows that the residual COD concentration varies with PH value of the solution. Low pH has been found effective for Fenton's reagent and the best removal efficiency is obtained at a pH of 3.

pH-value determination is necessary to remove inorganic carbons from wastewater because they can scavenge hydroxyl radicals. Inorganic carbons can be easily removed by controlling the pH to the acidic condition.

Effect of reaction time: The optimal reaction time is 90 min, as shown in Fig. 2. The results demonstrated that COD decrease gradually to 90 min. reaction time and then increase; this means that the reaction between ferrous iron and hydrogen peroxide with the production of hydroxyl radical was almost complete in 90 min.

Effect of Fe^{2+} and H_2O_2 addition: During Fenton process, iron and hydrogen peroxide are two major chemicals determining operation costs as well as efficacy.

Table 2: The optimum factors for treatment the leachate by Fenton process

Factor	pH	Reaction time (min)	H_2O_2/Fe^{2+} ratio	Temperature (°C)
Value	3.0	90	2.5:1	25

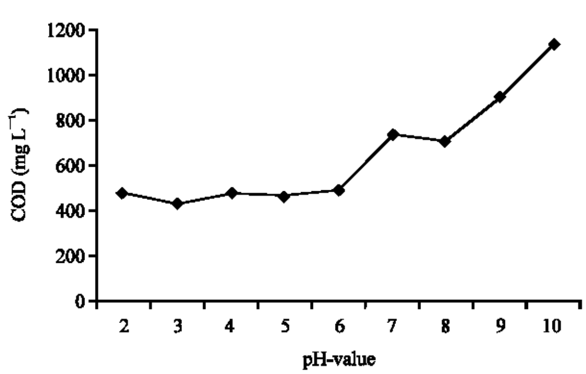

Fig. 1: The effect of pH on the COD removal by Fenton

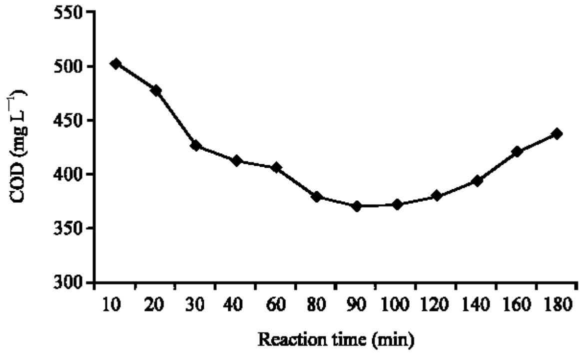

Fig. 2: The effect of reaction time on the COD removal

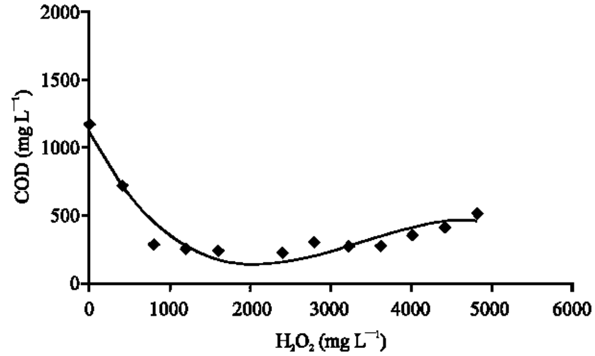

Fig. 4: The effect of H_2O_2 dosage on the COD removal

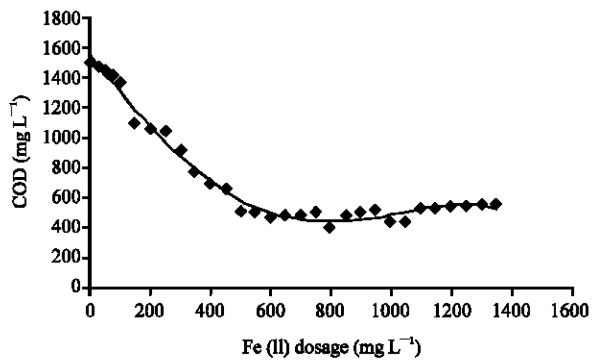

Fig. 3: The effect of Fe (II) dosage on the COD removal

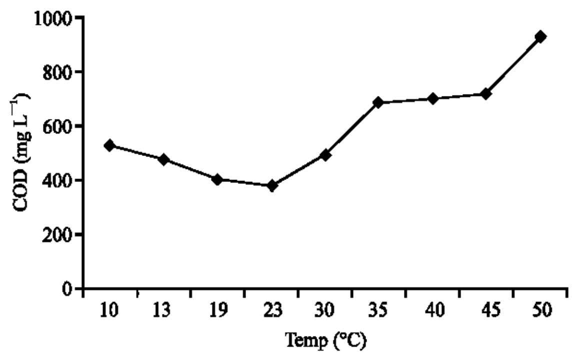

Fig. 5: The effect of Temp. on the COD removal

Determination of the favorable amount of the Fenton's reagent is highly important. H_2O_2 dosage depends heavily on initial COD. A high initial COD generally requires more H_2O_2. To investigate the optimum H_2O_2/Fe^{2+}, we studied the effect of Fe^{2+} and H_2O_2 addition separately.

Figure 3 (we added constant H_2O_2 equal 1665 mg L^{-1}) shows that the COD decreased with the increase amount of Fe^{2+} to 800 mg L^{-1} and then increased; the optimum amount of Fe^{2+} is 800 mg L^{-1}; then the optimum H_2O_2/Fe^{2+} ratio is 2.1:1, while in Fig. 4 (we added constant Fe^{2+} equal 800 mg L^{-1} (taken from Fig. 3) note with increase the amount of H_2O_2 lead to decrease COD t o (H_2O_2 = 2000 mg L^{-1}) and then increase; then the optimum H_2O_2/Fe^{2+} from this curve is 2.5:1. From the results above we took the optimum H_2O_2/Fe^{2+} equal 2.5:1.

H_2O_2 is more critical because it directly affects the theoretic maximum mass of $^{\bullet}OH$ generated.

The theoretical mass ratio of removable COD to H_2O_2 is 470.6/1000. That is, 1000 mg L^{-1} H_2O_2 theoretically removes 470.6 mg L^{-1} COD by oxidation. Occasionally, ç is used to evaluate the efficiency of H_2O_2 usage in the Fenton process: (Kang and Hwang, 2000).

$$\eta = 2.12\ COD_{oxi}/[H_2O_2] \qquad (3)$$

In Eq. 3, COD_{oxi} is the COD removed by oxidation. At a low H_2O_2 concentration relative to the COD concentration in the untreated leachate, ç may be above 100%, indicating that COD is primarily oxidized by $^{\bullet}OH$ radical instead of by H_2O_2 in conventional Fenton treatment ç decreases gradually below 100% with increasing [H_2O_2], indicating that remaining organics are refractory and unfavorably oxidized. (Kang and Hwang, 2000) In our study η = 64%, indicating that remaining organics are refractory.

Effect of temperature: Temperature is one of the important factors influencing catalytic oxidation reaction rates. Fig. 5 Showed that the COD decrease slightly as the temperature increase until temperature reach to 25°C and then decrease. The optimum temperature was 25°C to getting the better reaction.

CONCLUSIONS

Fenton treatment is currently the most cost-effective technologies available for reduction of COD and enhancement of biodegradability of landfill leachate. Both oxidation and coagulation contributed to COD reduction through Fenton treatment of leachate. Relative contributions depend primarily on pH, the ratio of Fenton regents and Fenton reagent dosages.

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

- The COD removal efficiency by oxidation was affected by the pH value. The most effective reaction was observed at (pH = 3.0).
- The reaction time of Fenton process was 90 min. to complete the reaction between ferrous sulfate and hydrogen peroxide.
- The optimum H_2O_2/Fe^{2+} was 2.5:1 according to the results of ferrous sulfate and hydrogen peroxide separately.
- The favorable reacting temperature is 25°C.

REFERENCES

Barbusiñski1, K. and K. Filipe, 2001. Use of Fenton's Reagent for Removal of Pesticides from Industrial Wastewater, Polish J. Environ. Studies, 10: 207-212.

Florida Center for Solid and Hazardous Waste Management, 2006. Options for Managing Municipal Landfill, Leachate: Year 1 Development of Iron-Mediated, Treatment Processes, State University System of Florida, University of Florida, Report No. 0432024-06, Florida, USA.

Gotvajn, A.Z. and Z.J. Konèan, 2005. Combination of Fenton and Biological Oxidation for Treatment of Heavily Polluted Fermentation Waste Broth, Acta Chimica. Slovenica., 52, 131-137 Res. Ch., 40: 463-474.

Kang, Y.W. and K.Y. Hwang, 2000. Effects of reaction conditions on the oxidation efficiency in the Fenton process, Water Res., 34: 2786-2790.

Lin, S.H. and C.C. Chang, 2000, Treatment of landfill leachate by combined electro-Fenton oxidation and sequencing batch rector method. Water Res., 34: 4243-4249.

Lopez, A., M. Pagano, A. Volpe and A.C.D. Pinto, 2004. Fenton's pre-treatment of mature landfill leachate. Chemosphere J., pp: 1005-1010.

Lopes de Morais, J. and P.P. Zamora, 2005. Use of advanced oxidation processes to improve the biodegradability of mature landfill leachates, J. Hazardous Materials, B123, pp: 181-186.

Yoon, J., J.S. Cho and S. Kim, 1998. The characteristics of coagulation of Fenton reaction in the removal of landfill leachate organics, Water Sci. Technol., 38: 209-214.

Zhang, H., H.J. Choi and C.P. Huang, 2005. Optimization of Fenton process for the treatment of landfill leachate, J. Hazardous Materials, B125, pp: 166-174.