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Pilot study on the advanced treatment of landfill leachate using a combined coagulation, fenton oxidation and biological aerated filter process

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ABSTRACT

Mature landfill leachate is typically non-biodegradable. A combination process was developed that includes coagulation, Fenton oxidation, and biological aerated filtering to treat biologically-produced effluent. In this process, coagulation and Fenton oxidation were applied in order to reduce chemical oxygen demand (COD) organic load, and enhance biodegradability. Poly-ferric sulfate (PFS) at 600 mg l^{-1} was found to be a suitable dosage for coagulation. For Fenton oxidation, an initial pH of 5, a total reaction time of 3 h, and an H_2O_2 dosage of 5.4 mmol l^{-1}, with a $(H_2O_2)/n(Fe^{2+})$ ratio of 1.2 and two-step dosing were selected to achieve optimal oxidation. Under these optimal coagulation and Fenton oxidation conditions, the COD removal ratios were found to be 66.67% and 56%, respectively. Following pretreatment with coagulation and Fenton oxidation, the landfill leachate was further treated using a biological aerated filter (BAF). Our results show that COD was reduced to 75 mg l^{-1}, and the color was less than 10 degrees.

1. Introduction

Landfill leachate is a type of wastewater that has a high concentration of organics. Biological methods are typically applied to treat this material (Ehrig and Stegmann, 1992). However, such methods are not effective for treating mature leachates (i.e., from landfills greater than 5–10 years of age), Leachates from mature landfills are usually characterized by a low BOD_5/COD ratio (normally <0.3) that contains a high fraction of refractory organics. Hence, further processing is required to treat the effluent that is released by biological reactions (Ho et al., 1974; Copa and Meidl, 1986; Amokrane et al., 1997; Chiang et al., 2001; Ushikoshi et al., 2002).

Recently, a number of methods have been explored to efficiently remove organics from leachate. These include membrane technologies (Ahn et al., 2002), electrochemical oxidation (Chiang et al., 1995), flotation (Zouboulis et al., 2003), ozone-activated carbon (Wu et al., 2004), coagulation/flocculation and ozonation (Rivas et al., 2003), O_3/H_2O_2 (Bila et al., 2005; Ntampou et al., 2006), photocatalysis (Wang et al., 2006), and the Fenton reaction (Cho et al., 2002).

In particular, the Fenton process has been extensively studied in recent years (Gau and Chang, 1996; Kim and Huh, 1997; Lin and Chang, 2000; Lau et al., 2002; Gulsen and Turan, 2004; Lopez et al., 2004). It is considered to be one of the most cost-effective options for treating landfill leachate (Pala and Erden, 2004). The Fenton process has a high removal efficiency for both apparent color and COD (Stephenson, 1997). This is because oxidation reactions are coupled with coagulation of organics due to the presence of ferrous/ferric ions. These metallic ions therefore have a dual character: they serve as both catalyst and coagulant. Moreover, in the Fenton process, the hydrogen peroxide reacts with ferrous ions to form a strong oxidizing agent (hydroxyl radical) with an oxidation potential of 2.8 V (Sarria et al., 2002). However, if only the Fenton process is applied to treat landfill leachate, the COD value cannot meet the new discharge standards of China's environmental regulations (less than 100 mg l^{-1}). In this study, a combined process of coagulation, Fenton oxidation, and biological aerated filtering was proposed to treat landfill leachate that is not biologically degradable using typical treatments.

Coagulation was used to remove suspend solids (SS) and colloids from the leachate. The operating cost of coagulation is low, and the process is widely used in wastewater treatment scenarios. The Fenton oxidation process, in which Fe^{2+} reacts with H_2O_2 to generate $\cdot OH$ (a powerful oxidizer), was employed to degrade organic pollutants. The typical Fenton wastewater treatment process features four stages: oxidation, neutralization, coagulation/flocculation and solid–liquid separation (Bigda, 1995; Englehardt et al., 2006). Organics are removed using both oxidation and coagulation, and Fenton oxidation can also be used to increase the biodegradability of landfill leachate.

Finally the organic matter removed by the biological aerated filter (BAF), which incorporated an inert medium to support biomass and remove suspended solids (Pujol et al., 1994; Gogate and Pandit, 2004). This was used as an alternative to the traditional activated sludge process. BAF is very effective in removing SS, COD,

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BOD, and ammonia, especially from wastewater that features low levels of SS and COD.

With the combination process that comprises coagulation, Fenton oxidation pretreatment, and BAF end-stage treatment, landfill leachate was successfully treated and the optimal treatment conditions were obtained.

2. Materials and methods

2.1. Characteristics of leachate

Landfill leachate was collected from a landfill in Jiangmen city, Guangdong Province, PR China. The landfill is about 10 years old. The leachate was treated by sequence batch reactor (SBR), with the SBR effluent characteristics as follows: COD (mg l^{-1}) = 600–700, BOD_5(mg l^{-1}) = 3–9, NH_3–N (mg l^{-1}) < 3, pH = 5–8, and color (degrees) = 400–800. The BOD_5/COD ratio of effluent from SBR was about 0.01. Both the COD and the color failed to meet the new Chinese pollution discharge standards.

2.2. Experimental methods and apparatus

Three steps were conducted to treat the leachate: (1) flocculation (2) Fenton treatment, and (3) BAF treatment.

Flocculation was conducted according to the following procedure: Wastewater was decanted into 50 l reaction vessels. A specific amount of coagulant was added, and the leachate was stirred at an initial mixing rate of 200 rpm for 5 min, and then at about 50 rpm for 2 min. Finally, the sample was allowed to settle without stirring for half an hour. The water in the upper clear layer was sampled to measure COD values and color.

Fenton treatment was conducted according to following procedure: First, ferrous sulfate ($FeSO_4 \cdot 7H_2O$) was added to the 50 l reaction vessels. Subsequently hydrogen peroxide solution (H_2O_2, 30%, w/w) was added rapidly under vigorous stirring. After a predefined oxidation period, calcium oxide (CaO) was added to the solution during vigorous stirring, to adjust the pH to approximately 6.5. Sodium hydroxide (NaOH) solution was added to adjust the pH to 8.0, followed by the addition of a small amount of polyacrylamide (PAM, 0.2%, w/w) for flocculation. The solution was allowed to settle for 30 min. Finally, the water in the upper clear layer was sampled to measure COD values.

The size of the BAF cylinder was Φ200 mm$*$H2000 mm, and the BAF vessels were ceramic and ranged in size from 3 mm to 5 mm. The hydraulic retention time (HRT) was adjustable consistent with flow rate. The ratio of aeration gas to water was 5:1.

All samples in our experiments were measured using standard methods (OECD, 1981).

Fig. 1 shows the processes of coagulation, Fenton oxidation, and BAF. Following coagulation and Fenton oxidation, the wastewater was fed into an up-flowing BAF column, where oxygen was supplied by an aeration blower.

3. Results and discussion

3.1. Coagulation process

The SBR effluent of the landfill leachate was separately treated with polymeric aluminum (PAC, 8%, w/w) and polyferric sulfate (PFS, 10%, w/w). The color of landfill leachate was 200 degrees and 40 degrees after treatment with PAC and PFS, respectively. The change in COD as a result of the treatment is shown in Fig. 2.

3.1.1. Effects of the coagulant on COD removal

Fig. 2 clearly shows that the coagulant had a definite impact on COD removal efficiency. COD removal in the sample treated with PFS was better than that in the sample treated with PAC. The PFS

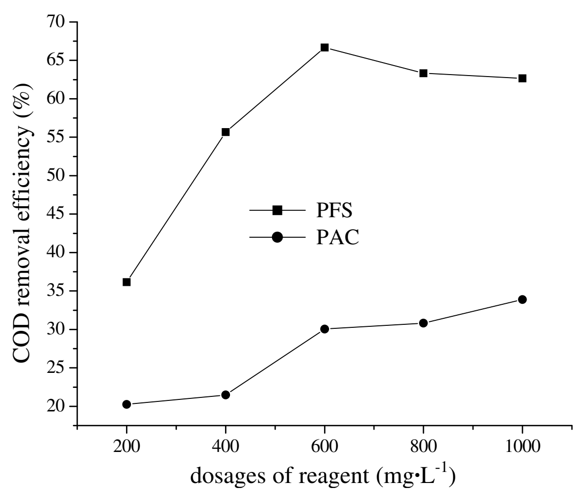

Fig. 2. Effect of coagulant dosing on COD removal efficiency.

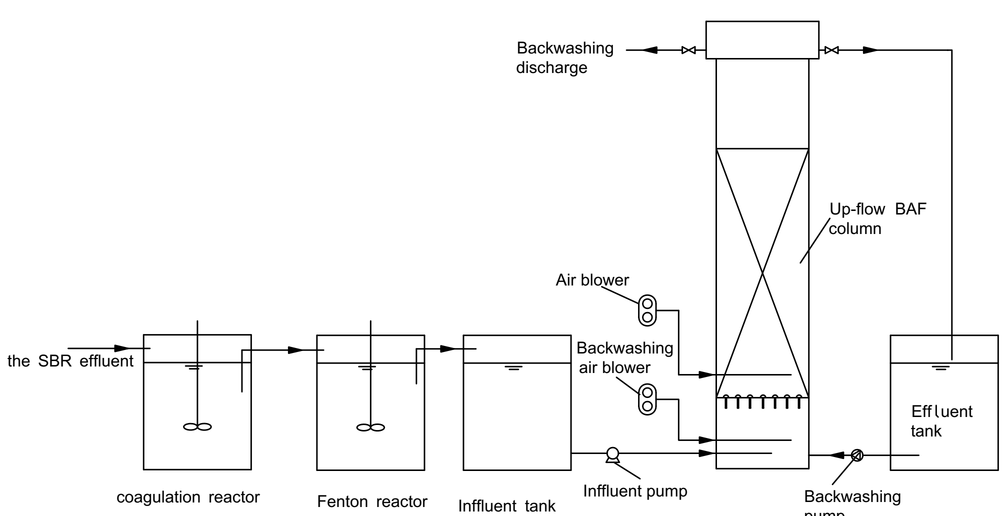

Fig. 1. Schematic view of the pilot plant.

dosage also impacted the COD removal efficiency, and the maximum COD removal efficiency reached 66.7% at the point when the dosage of PFS was 600 mg l^{-1}.

3.1.2. Effect of coagulant on color removal

The color removal rates were monitored while the samples were treated with PAC at 1000 mg l^{-1} and with PFS at 600 mg l^{-1}. When treated with PFS, the color removal rate was much better than that with PAC of the effluent with its original color of 400 degrees. The removal rate extended as high as 90%.

In terms of the COD and color removal efficiency, PFS was generally better than PAC. The cost of the PFS treatment was also lower, at 1 yuan RMB (about 0.15 USD) per ton of wastewater, while the cost of treatment with PAC was 1.2 yuan RMB (about 0.18 USD) per ton. Thus PFS was a better coagulant for the advanced treatment of this landfill leachate.

3.2. Fenton oxidation process

The effects of the initial pH and the dosages of hydrogen peroxide (H_2O_2) and $FeSO_4 \cdot 7H_2O$ on the effectiveness of the Fenton oxidation process were studied.

3.2.1. Effect of the initial pH

The effect of the initial pH on COD removal efficiency was as shown in Fig. 3. With 5.4 mmol l^{-1} H_2O_2 and 4.5 mmol l^{-1} Fe^{2+}, the maximum COD oxidation-based removal efficiency occurred at pH 3–5, and the COD removal efficiency was over 45%. At an extremely low pH (<3), the COD removal efficiency decreased sharply, principally due to the lower reaction rate of $[Fe(H_2O)]^{2+}$ and H_2O_2 (Lidia et al., 2001), increased scavenging of OH by H^+ (Gallard et al., 1998), and inhibition of the reaction between Fe^{3+} and H_2O_2 due to high concentrations of H^+ (Tang and Huang, 1996). By contrast, COD removal efficiency dropped significantly as the pH exceeded 5.0, due to the increasing rate of auto decomposition of H_2O_2, deactivation of iron ions into iron oxyhydroxides, and the decreased oxidation potential of·OH. Therefore, COD removal efficiency depends strongly on the initial pH of the solution.

The pH of the landfill leachate after coagulation was about 5 and it dropped to 3–4 when Fe^{2+} and H_2O_2 were added. This pH value was consistent with the Fenton oxidation conditions and as a result the initial pH was not changed for the Fenton oxidation following coagulation.

3.2.2. Dosages of Fenton reagents

The effect of the $n(H_2O_2)/n(Fe^{2+})$ ratio on COD removal efficiency was examined when the dosages of $[Fe^{2+}]$ were 2 mmol l^{-1}, 4 mmol l^{-1}, and 6 mmol l^{-1}. The initial pH was 5.0 and the results are shown in Fig. 4. At the three dosages of Fe^{2+}, the maximum oxidative COD removal efficiency always occurred at $n(H_2O_2)/n(Fe^{2+}) = 1.2$, reaching 48.5% at $Fe^{2+} = 6$ mmol l^{-1}. The oxidation efficiency dropped when the $n(H_2O_2)/n(Fe^{2+})$ ratio increased further. This result was attributed to the scavenging effect of peroxide on the hydroxyl radicals, which presumably became stronger as the ratio $n(H_2O_2)/n(Fe^{2+})$ rapidly increased, as shown in Eq. (1):

$$H_2O_2 + {}^{\cdot}OH \rightarrow H_2O + {}^{\cdot}HO_2 \quad (1)$$

Oxidation efficiency dropped sharply to one half of the maximum at a ratio $n(H_2O_2)/n(Fe^{2+}) < 1.2$, due to the increasing scavenging effect of Fe^{2+} on hydroxyl radicals, as shown in Eq. (2):

$$^{\cdot}OH + Fe^{2+} \rightarrow Fe^{+3} + OH \quad (2)$$

These results show that the optimal $n(H_2O_2)/n(Fe^{2+})$ ratio was approximately 1.2 to oxidize this leachate.

The hydrogen peroxide dosage played an important role in organic degradation. The COD removal efficiency of three times increased with H_2O_2 concentration (Fig. 5). When the H_2O_2 dosage increased from 1.8 to 5.4 mmol l^{-1} (while the dosage of Fe^{2+} increased from 1.5 to 4.5 mmol l^{-1}), the COD removal efficiency increased from 20% to 48.5%, but further addition did not significantly increase the COD removal efficiency. These results suggest that the optimal dosage of $n(H_2O_2)$ was approximately 5.4 mmol l^{-1} to oxidize this leachate.

3.2.3. Effect of dosing time

H_2O_2 and Fe^{2+} were dosed twice under a $n(H_2O_2)/n(Fe^{2+})$ ratio of 1.2. The 2.7 mmol l^{-1} H_2O_2 and 2.25 mmol l^{-1} Fe^{2+} were dosed first, and these were followed by a second dose 1.5 h later. The total dose was the same and the total reaction time remained at 3 h.

The effect of dosing time on COD removal efficiency in the context of the Fenton reaction is shown in Fig. 6. As the dosing time increased from one to two, COD removal efficiency increased from 45% to 56%. The COD removal efficiency of three times increased only slightly. Consequently, the twice-dosing schedule was preferred to achieve higher removal efficiency and to promote ease of operation.

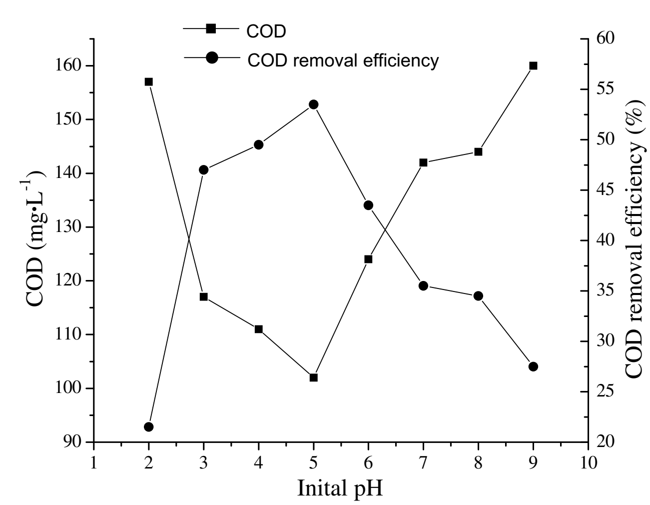

Fig. 3. Effect of initial pH on COD removal efficiency (total reaction time = 3 h; initial COD = 220 mg l^{-1}; H_2O_2 = 5.4 mmol l^{-1}; Fe^{2+} = 4.5 mmol l^{-1}).

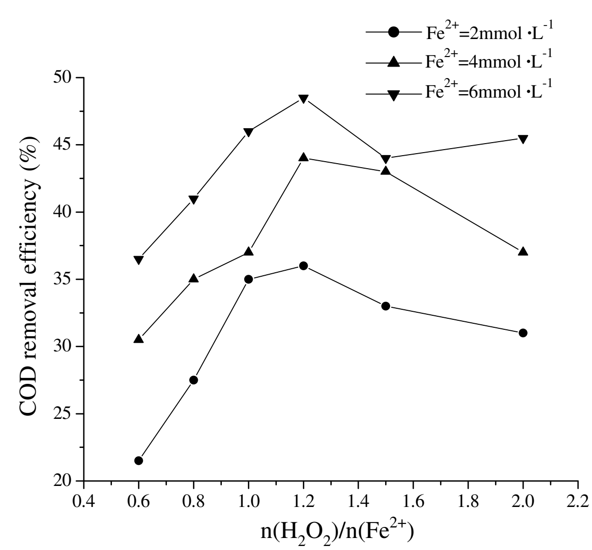

Fig. 4. The effect of $n(H_2O_2)/n(Fe^{2+})$ ratio on COD removal efficiency (conditions: initial pH 5; reaction time = 3 h; original COD = 220 mg l^{-1}).

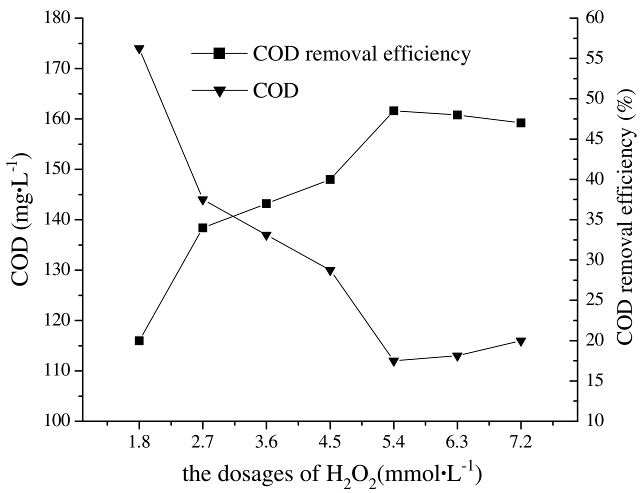

Fig. 5. Effect of H_2O_2 dosing on COD removal efficiency (conditions: initial pH 5; reaction time = 3 h; original COD = 220 mg l^{-1}; $n(H_2O_2)/n(Fe^{2+})$ ratio = 1.2).

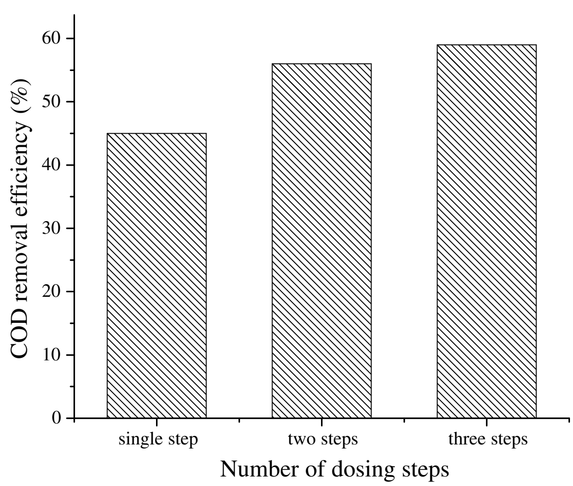

Fig. 6. Effects of dosing times on COD removal efficiency in Fenton oxidation of the leachate (conditions: initial pH 5; reaction time = 3 h; original COD = 220 mg l^{-1}; H_2O_2 = 5.4 mmol l^{-1}; $n(H_2O_2)/n(Fe^{2+})$ ratio = 1.2).

The optimum experimental conditions for the Fenton leachate oxidation process were shown to be as follows: pH = 5 (the pH of the original wastewater after coagulation), H_2O_2 = 5.4 mmol l^{-1}; and $n(H_2O_2)/n(Fe^{2+})$ ratio = 1.2, all with a twice-dosing schedule. Under these conditions the COD removal efficiency was 56%, and the color was less than 10 degrees after Fenton oxidation.

3.3. Coagulation, Fenton oxidation and BAF process

The effect of BAF hydraulic retention time (HRT) on COD removal efficiency was studied following coagulation and Fenton oxidation. The experimental results are as shown in Fig. 7. In Fig. 7, when the HRT was 3 h, the average effluent COD was about 92 mg l^{-1}, and the average COD decreased to 75 mg l^{-1} as the HRT was extended to 4.5 h. The average COD was nearly the same as that associated with the 5.5 h HRT.

4. Economic and technical analysis

The total cost of treatment for this landfill leachate comprises the cost of the flocculation process, which was 1 yuan RMB per ton, the cost of the Fenton process at 2.5 yuan RMB per ton and

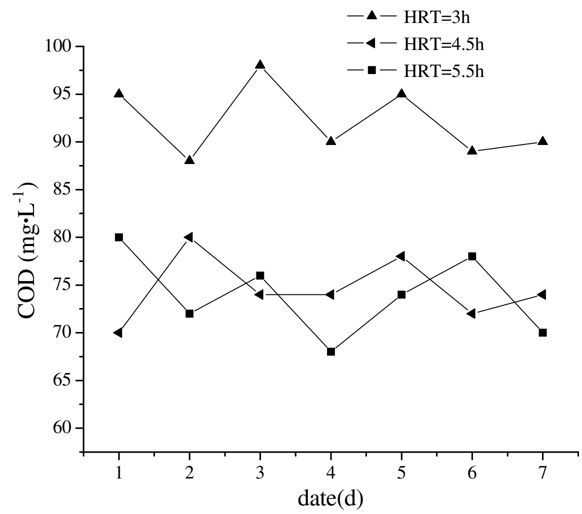

Fig. 7. Effects of hydraulic retention time on COD removal efficiency in BAF treatment (conditions: coagulation process: PFS = 600 mg l^{-1}, reaction time = 1 h; Fenton oxidation process: initial pH 5; reaction time = 3 h; H_2O_2 = 5.4 mmol l^{-1}; $n(H_2O_2)/n(Fe^{2+})$ ratio = 1.2, influent COD = 100–130 mg l^{-1}).

the BAF process cost which was 0.2 yuan RMB per ton. The volume of sludge created by these processes was 0.2 ton per ton of leachate. Under normal circumstances, this material can be pumped back into the landfill at negligible cost. Therefore, the total cost was 3.7 yuan RMB (0.60 USD) per ton.

5. Conclusions

(1) A combined process that includes coagulation, Fenton oxidation, and biological aerated filtering showed excellent treatment results in COD removal efficiency and in color removal of landfill leachate following SBR treatment.
(2) After coagulating with PFS, COD removal efficiency reached as high as 66.7%. The color of the effluent was reduced to 40 degrees at dosages of 600 mg l^{-1}.
(3) The optimal conditions for the Fenton oxidation process were as follows: original pH = 5, $n(H_2O_2)/n(Fe^{2+})$ ratio = 1.2, H_2O_2 = 5.4 mmol l^{-1}, all with a two-phase dosing schedule. Under these conditions, COD removal efficiency was 56.0% and the color of the effluent was less than 10 degrees.
(4) In the BAF process, HRT played a key role in COD removal. When the HRT value was 4.5 h, it was possible to reduce the COD of the effluent down to 75 mg l^{-1}, thereby meeting the new discharge standards set forth by China's EPA.

The total cost was 3.7 yuan RMB (0.60 USD) per ton of wastewater. This is a relatively low treatment cost for landfill leachate.

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