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Combined treatment of the municipal landfill leachate by fluidized bed Fenton process

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ABSTRACT

Compared to the incineration and composting, landfill was an ordinary technology which is often used in the solid waste disposal. Landfill leachate is highly loaded, toxic, and harmful to the sanitation of wastewater. In past 20 years, technologies such as advanced oxidation processes had been developed for the treatment of wastewater which is contaminated by the hazardous and recalcitrant organic compounds, such as pesticides, surfactants, and pharmaceuticals and endocrine disrupting chemicals, but so far there is little information about the application of fluidized-beds Fenton process in the oxidation treatment of organic compounds from the municipal landfill leachate. In this paper, the effects of different treatments to the municipal landfill leachate from Shaoxing landfill by gas–liquid fluidized bed with Fenton reagent were examined and evaluated. The effects of various operating conditions, such as treatment time, initial COD strength, initial pH value, initial $[H_2O_2]$, initial $[Fe^{2+}]$, and ventilation volume were examined. After evaluation, several optimal operating conditions (COD = 2500 mg/L, reaction time of 30 min, pH = 2.5, $[Fe^{2+}]_0 = 0.05$ mmol/L, $[H_2O_2]_0 = 0.075$ mmol/L, ventilation volume of 0.12 m^3/h, and temperature = 60˚C) were found under which the maximum COD removal rate (61.4%) was obtained.

Keywords: Municipal landfill leachate; Treatment; Fluidized bed; Fenton

1. Introduction

Landfill, compared to other technologies, such as incineration and composting, was a common method to dispose of solid waste. It was reported that almost 90% of the municipal solid waste in China is disposed in landfills [1]. Landfill leachate, which came from the waste degradation in landfill sites, especially those from aged landfill sites, brought many problems for complete treatment economically both by biological and physicochemical methods. The main hazards of aged landfill leachate are the high levels of ammonium, high organic matter contents with nonbiodegradable organic substances, such as humic type of constituents, etc. As a result, the surface water around the landfill sites can be easily contaminated by the landfill leachate. For instance, it was reported that the surface water was severely polluted by the landfill site which was 4 km away from the investigation site. Moreover, it was found that the landfill leachate can contaminate groundwater even at 60 m under the ground [2–4].

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In the past 20 years, advanced oxidation processes (AOPs) have already been developed for the treatment of wastewater containing hazardous and recalcitrant organic compounds (such as pesticides, surfactants, and pharmaceuticals and endocrine disrupting chemicals) [5]. AOPs have also been successfully used as pre-treatment methods to reduce the concentrations of toxic organic compounds that inhibit biological wastewater treatment processes. A great number of methods were classified under the broad definition of AOPs based on the oxidizing agents applied. Most of them use a combination of strong oxidizing agents (e.g. H_2O_2, O_3) with catalysts (e.g. transition metal ions) and irradiation (e.g. ultraviolet, visible) [6–8]. Among these methods, the Fenton process has been one of the most popular technologies for wastewater treatment [9–11]. However, the Fenton process produces a large amount of ferric hydroxide ($Fe(OH)_3$) sludge, which requires additional separation and disposal. The disadvantages of Fenton process have limited its further application in treating wastewater. To cope with this problem, the fluidized bed Fenton process has been developed to reduce the production of iron sludge [12].

The various Fenton technologies, such as photo-Fenton, electron-Fenton, and fluidized bed Fenton processes have already been evaluated for degradation of a number of organic pollutants [13]. Multiphase gas–liquid–solid fluidized bed reactors have been widely used in all types of research, such as physics, chemistry, energy, environment, medicine, and materials [14–17]. The advantages of the fluidized bed reactors are excellent mass and heat transfer characteristics, high rate of reaction resulting from the close contact between the different phases, and the continuous operation [18]. According to the previous literatures, the application of fluidized-beds Fenton process in the oxidation treatment of organic compounds from the municipal landfill leachate has not been studied extensively yet. Therefore, in this study, the effects of different treatments to the municipal landfill leachate from Shaoxing landfill site were compared by using gas–liquid fluidized bed with Fenton reagent. Various operating conditions, such as treatment time, initial pH value, initial COD strength, initial [H_2O_2], initial [Fe^{2+}], temperature and ventilation volume were examined and evaluated, accordingly.

2. Materials and methods

2.1. Municipal landfill leachate

The municipal landfill leachate was obtained from Shaoxing landfill site at Shaoxing, P.R. China. A 100 L leachate sample was obtained from a wastewater pond in the landfill site. Then, it was filtered through a glass fiber filter to remove coarse suspended solids. The municipal landfill leachate characteristics were shown in table 1.

Table 1
The municipal landfill leachate characteristics (mg/L)

pH	COD	BOD_5	NH_3-N	TOC	SS
7.5	2,500	550	1,500	820	730

2.2. Experimental apparatus

The gas–liquid fluidized bed reactor was composed of a plexiglass column with a diameter of 50 mm and a height of 2,000 mm. It was equipped with a gas–liquid distributor at the bottom, and a round water bath surrounding the column. The gas–liquid distributor was connected to the gas compressor through a gas flow meter. A buffer tank was also included to prevent back-flashing of air and fluid in the reactor. Air flows through gas–liquid distributor to the reaction column to form air bubbles in diameter of about 2 mm.

2.3. Experimental methods

The municipal landfill leachate samples were transferred to the fluidized bed Fenton process. After the cylinder reached to the constant temperature, the oxidant was added, and the pH value in solution was adjusted to a predetermined value. Air was then compressed through and flew through the bottom of the column, and the flow rate was adjusted to form bubbles with a diameter of 2 mm. Samples were taken as predetermined intervals and were analyzed.

2.4. Analytical methods

The value of pH was measured with a pH probe, according to APHA Standard Method. COD was measured by model MS-3 microware digestion system [19]. All experiments were performed thrice. The data of the results were the mean. The value of standard deviation was calculated by Excel Software.

3. Results and discussion

3.1. Effect of reaction time on COD removal rate

The effect of reaction time on COD removal rate was tested to determine an optimal treatment condition for further research. Fig. 1 depicted a typical

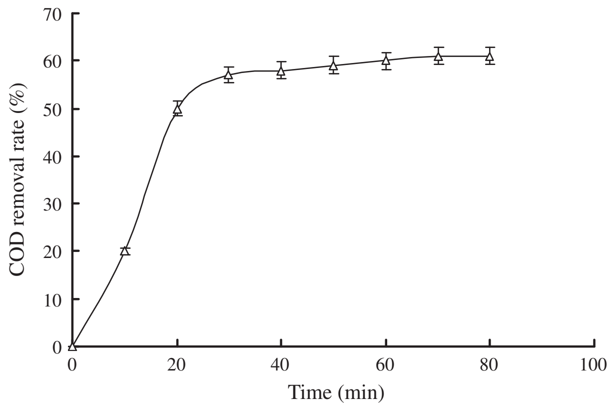

Fig. 1. Effect of reaction time on COD removal rate. Experimental conditions: COD = 2,500 mg/L, pH = 3, $[H_2O_2]_0$ = 0.075 mmol/L, $[Fe^{2+}]_0$ = 0.05 mmol/L, ventilation volume of 0.12 m^3/h, and temperature = 60℃.

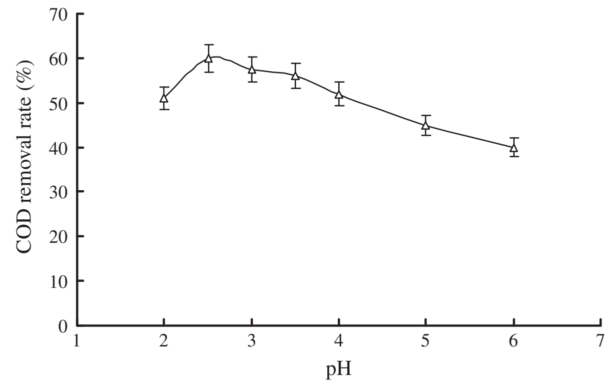

Fig. 2. Effect of pH value on COD removal rate. Experimental conditions: COD = 2,500 mg/L, reaction time of 30 min, $[H_2O_2]_0$ = 0.075 mmol/L, $[Fe^{2+}]_0$ = 0.05 mmol/L, ventilation volume of 0.12 m^3/h, and temperature = 60℃.

reaction curve showing the COD removal rate of the municipal landfill leachate changes with reaction time. The results demonstrated that organic compounds from the municipal landfill leachate were rapidly degraded by fluidized bed Fenton process. Most organic compounds removal occurred in the first 30 min. After 30 min, the decrease of residual organic compounds became insignificant. More foam was observed as the oxidation proceeded, which indicated the formation of carbon dioxide. The COD removal rate was about 61.4% at 30 min. Based on the result, the reaction time for fluidized bed Fenton process was determined to be 30 min for further experiments.

3.2. Effect of pH value on COD removal rate

The pH value of the solution has a great impact on the COD removal rate. The pH value affected the activity of both the oxidant and the substrate, the speciation of iron, and hydrogen peroxide decomposition. It can be explained that higher hydroxyl radical product yields in the pH range of 2–4 by a reaction involving organometallic complex where either hydrogen peroxide was regenerated or reaction rates were increased [20]. Fig. 2 showed the effect of the pH value in solution on the COD removal rate. Either too high or too low pH value caused low COD removal rate. The pH value between 2.0 and 3.0 had been found effective, and the best COD removal rate was obtained at the pH 2.5. According to previous literature, optimal pH values were reported for landfill leachate treatment by Fenton process range from 2.0 to 4.5 [21]. At low pH, the reaction would be slowed down because hydrogen peroxide stays stable and solvates a proton to form an oxonium ion (e.g. $H_3O_2^+$). An oxonium ion made hydrogen peroxide electrophilic to enhance its stability and presumably reduces the reactivity with ferrous ion substantially. At the same time, the formed complex species $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ also reacted more slowly with hydrogen peroxide. In addition, the scavenging effect of the $HO^•$ radical by H^+ was severe. On the other hand, at high pH, the oxidation efficiency rapidly decreased, not only by decomposition of hydrogen peroxide, but also by deactivation of a ferrous catalyst with the formation of ferric hydroxide complexes leading to a reduction of $HO^•$ radical [21].

3.3. Effect of $[Fe^{2+}]$ on COD removal rate

In Fenton process, iron and hydrogen peroxide were two major chemicals determining operation costs as well as efficacy. Determination of the favorable amount of the Fenton's reagent was highly important. Fig. 3 shows the effect of initial $[Fe^{2+}]$ to the COD removal rate. The initial $[Fe^{2+}]$ concentration range from 0 to 0.4 mmol/L. From Fig. 3, it can be seen that the COD removal rate increased with increasing initial $[Fe^{2+}]$ concentration. It may be explained by the possibility of occurrence of redox reactions, since $HO^•$ radicals are scavenged by the reaction with the hydrogen peroxide or with another Fe^{2+} molecule as below. The inefficient COD removal rate capacity with low Fe^{2+} concentration was probably due to the insufficient $HO^•$ radical production for the oxidation [22].

3.4. Effect of $[H_2O_2]$ on COD removal rate

Fig. 4 shows the relationship between the COD removal rate and the initial concentration of H_2O_2. Increasing the concentration of H_2O_2 from 0.025 to 0.075 mmol/L significantly promote the degradation

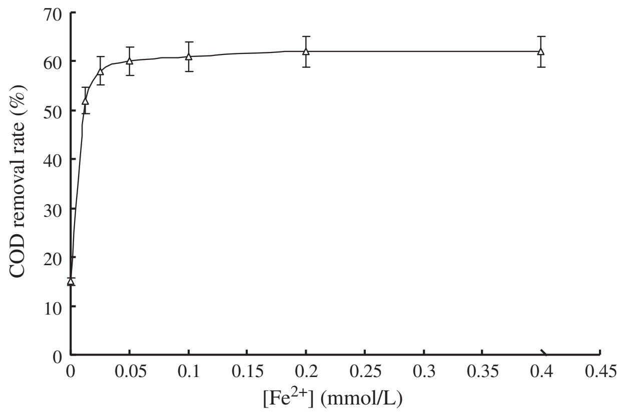

Fig. 3. Effect of initial $[Fe^{2+}]$ on COD removal rate. Experimental conditions: COD = 2,500 mg/L, reaction time of 30 min, pH = 2.5, $[H_2O_2]_0 = 0.075$ mmol/L, ventilation volume of $0.12\,m^3/h$, and temperature = 60℃.

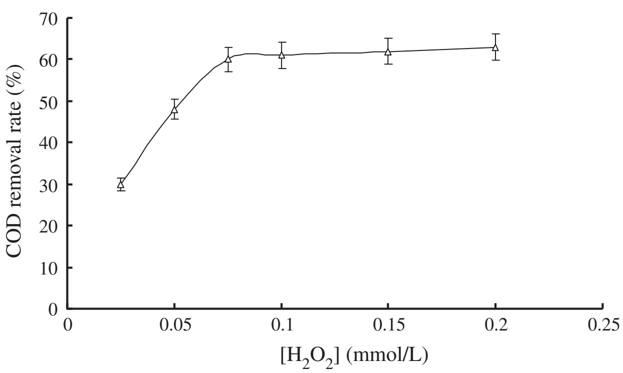

Fig. 4. Effect of initial $[H_2O_2]$ on COD removal rate. Experimental conditions: COD = 2,500 mg/L, reaction time of 30 min, pH = 2.5, $[Fe^{2+}]_0 = 0.05$ mmol/L, ventilation volume of $0.12\,m^3/h$, and temperature = 60℃.

of organic compounds from the municipal landfill leachate. This was due to the oxidation power of Fenton process which was improved with increasing $HO^{\bullet}$ radical amount in solution obtained from the decomposition of increasing hydrogen peroxide. However, too much H_2O_2 (from 0.075 to 0.2 mmol/L) caused no significant change in COD removal rate. This may be due to the fact that $HO^{\bullet}$ radicals would be scavenged under high H_2O_2 concentration (Eqs. 1) [23]:

$$HO_2^{\bullet} + HO^{\bullet} \rightarrow H_2O + O_2 \tag{1}$$

3.5. Effect of ventilation volume on COD removal rate

Fig. 5 illustrates the effect of the gas flow rate on the COD removal rate. It was found that the COD removal rate changed with the flow rate. When the gas flow rate was below $0.12\,m^3/h$, the COD removal rate increased with the increasing flow rate. However, when the gas flow rate was above $0.12\,m^3/h$, the COD removal rate decreased. When the gas flow rate further increased, the fluidized bed was in a completely liquidized state, and heat and mass transfer were optimized. However, when the gas flow rate became too high, the tunnel effect reduced the mass transfer process, and consequently decreased the COD removal rate [24].

3.6. Effect of temperature on COD removal rate

Temperature was one of the most important factors that influence the catalytic oxidation reaction rates. In principle, the removal of organic maters in Fenton treatment of landfill leachate had positively correlated with temperature. However, over high temperature would cause inefficient H_2O_2 decomposition and offsets of COD removal. It should be noted that the increase of organic removal due to elevation of temperature is relatively small compared to other treatment conditions [25]. In this paper, in order to investigate the effect of temperature, a series of experiments were conducted by varying temperature from 30 to 80℃. Fig. 6 demonstrated the effect of temperature on the COD removal rate. It was noticed that, when the temperature was below 60℃, the COD removal rate increased with increasing temperature. Whereas, the COD removal rate decreased when the temperature was above 60℃. In general, the rate of chemical reaction was positively correlated with temperature because of the increase of average kinetic energy of the molecules. High temperature was initially helpful to activate the $HO^{\bullet}$ radicals and beneficial for organic compounds removal. However, over high temperature would lead to the decomposition of H_2O_2 into O_2 and H_2O.

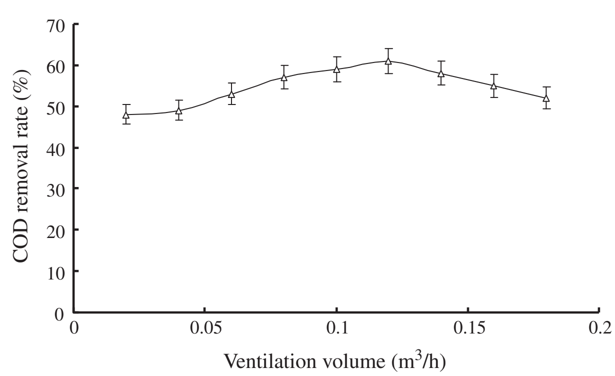

Fig. 5. Effect of ventilation volume on COD removal rate. Experimental conditions: COD = 2,500 mg/L, reaction time of 30 min, pH = 2.5, $[H_2O_2]_0 = 0.075$ mmol/L, $[Fe^{2+}]_0 = 0.05$ mmol/L, and temperature = 60℃.

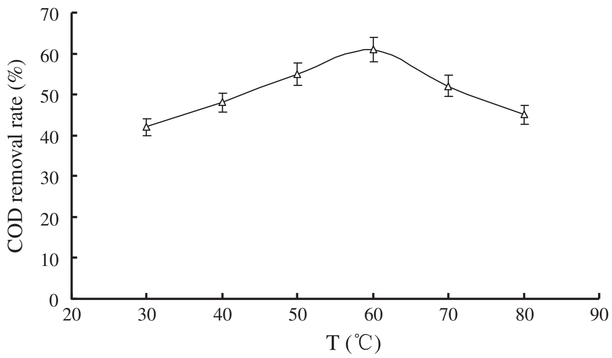

Fig. 6. Effect of temperature on COD removal rate. Experimental conditions: COD = 2,500 mg/L, reaction time of 30 min, pH = 2.5, $[H_2O_2]_0$ = 0.075 mmol/L, $[Fe^{2+}]_0$ = 0.05 mmol/L, and ventilation volume of 0.12 m^3/h.

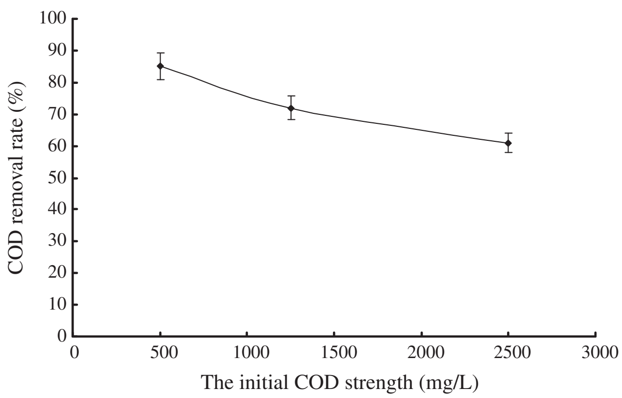

Fig. 7. Effect of the initial COD strength. Experimental conditions: reaction time of 30 min, pH = 2.5, $[H_2O_2]_0$ = 0.075 mmol/L, $[Fe^{2+}]_0$ = 0.05 mmol/L, ventilation volume of 0.12 m^3/h and temperature = 60℃.

3.7. Effect of the initial COD strength

The amount of Fenton's reagent is necessary for an effective treatment depended on the initial COD strength. This can differ depending on whether the Fenton process had a role of pretreatment or ultimate pretreatment. Bowers et al. [26] found that a primary or acceptable degradation may occur in a relatively low consumption and be much more efficient than ultimate degradation. The tests about the effect of the initial COD strength was carried out under the reaction time of 30 min, pH = 2.5, $[H_2O_2]_0$ = 0.075 mmol/L, $[Fe^{2+}]_0$ = 0.05 mmol/L, ventilation volume of 0.12 m^3/h and temperature = 60℃. From Fig. 7, it is shown that more COD was removed at higher COD strengths than lower COD with the same amount of dosage though COD removal rate decreased with the increasing initial COD strength. This indicated that the by-products of oxidation reactions were mainly made of short chain organic acids that were difficult to be further oxidized [27].

4. Conclusions

The effects of treatment conditions to the fluidized bed Fenton process were evaluated through the treatment of the organic compounds from the municipal landfill leachate. The optimal treatment condition was determined as follows: COD = 2,500 mg/L, reaction time of 30 min, pH = 2.5, $[Fe^{2+}]_0$ = 0.05 mmol/L, $[H_2O_2]_0$ = 0.075 mmol/L, ventilation volume of 0.12 m^3/h, and temperature = 60℃. Under this condition, the maximum COD removal rate reached 61.4% which confirm the notion that COD removal efficiencies range from 45 to 85% mainly depended on landfill leachate characteristic and dosages of Fenton reagents [28]. It was proved that the organic compounds from the municipal landfill leachate could be treated effectively using fluidized bed Fenton process.

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