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Research Article

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Degradation of organic compounds by fluidized bed fenton process

Muqing Qiu[1], Jianxin Shou[2*] and Yanni Lu[2]

[1]College of Life Sciences, Shaoxing University, Shaoxing, Zhejiang, P.R. China
[2]Department of Life Science, Shaoxing University Yuanpei College, Shaoxing, Zhejiang, P.R. China

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ABSTRACT

Landfill leachate is highly loaded, toxic and is bad for the sanitation of wastewater. In this paper, the treatment of the municipal landfill leachate from Shaoxing landfill was evaluated by using gas-liquid fluidized bed with Fenton reagent. The effects of various operating conditions such as treatment time, initial pH value, initial [H_2O_2], initial [Fe^{2+}], and ventilation volume were examined. It was found that the optimal operating conditions existed as: COD=2500mg/L, reaction time of 30min, pH=2.5, $[Fe^{2+}]_0$=0.05mmol/L, $[H_2O_2]_0$=0.075mmol/L, ventilation volume of 0.12m^3/h, and temperature=60□. Under these conditions, 61% COD removals rate were obtained.

Key words: Organic compounds; Degradation; Fluidized bed Fenton

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INTRODUCTION

Landfilling, compared to other technologies such as incineration and composting, is a common way to dispose of solid waste. It is reported that about 90% of the municipal solid waste (MSW) is disposed of in landfills in China[1]. Landfill leachate, comes from the waste degradation in landfill sites, especially those from aged landfill sites, has been a challenge for complete treatment economically by both biological or combined treatment with physicochemical methods. The focuses of old landfill leachate treatments are the significant amount of ammonium, high organic matter contents with nonbiodegradable organic substances, such as humic type of constituents, etc. [2].

Advanced oxidation processes (AOPs) have already been used for the treatment of wastewater containing hazardous and recalcitrant organic compounds such as pesticides, surfactants, and pharmaceuticals and endocrine disrupting chemicals[3]. They have also been successfully used as pretreatment methods to reduce the concentrations of toxic organic compounds that inhibit biological wastewater treatment processes. A great number of methods are 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)[4,5]. Among chemical methods, especially advanced oxidation process, such as photocatalytic oxidation, photo-Fenton, electro-Fenton, UV/ H_2O_2, and ozonation processes eem to be more promising[6]. These processes base on generation of powerfully oxidizing radicals (especially •OH). Degradation of azo dye by Fenton type processes could be significally accelerated in the presence of UV irradiation, resulting with complete mineralization of the azo dye[7]. The use of TiO_2 as semiconductor photocatalysts for environmental clean up promises increasing attention because of its low cost, non-toxic, insolube, highly reactive nature and relatively high chemical stability of TiO_2, especially when sunligh is used as the source of irradiation[8]. Photocatalytic methods with catalysts was successfully applied to the decompositon of many organic contaminants, i.e. including azo dyes[9].

The Fenton technologies such as photo-Fenton, electron-Fenton, and fluidized bed Fenton processes have been already investigated for degradation of a number of organic pollutants [10]. 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[11-13]. The advantages of the fluidized bed reactors have been proved as its excellent mass and heat transfer characteristics, high rates of reaction resulting from the close contact between the different phases, and the continuous operation [14]. The application of fluidized-beds Fenton process in the oxidation treatment of organic compounds from the municipal landfill leachate has not been studied extensively.

Therefore, in this study, the treatment of the municipal landfill leachate from Shaoxing landfill site was evaluated by using gas-liquid fluidized bed with Fenton reagent. The effects of various operating conditions such as treatment time, initial pH value, initial [H_2O_2], initial [Fe^{2+}], temperature and ventilation volume were examined.

EXPERIMENTAL SECTION

2.1 Municipal landfill leachate

The municipal landfill leachate was obtained from Shaoxing landfill site at Shaoxing, P.R. China. A 100L 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 on average were pH=7.5, COD=4600mg/L, BOD_5=550mg/L, NH_3-N=1500mg/L, TOC=820mg/L, SS=730mg/L . In this study, the municipal landfill leachate samples were diluted to the desired COD strengths (2500mg/L) with distilled water, and transferred to the fluidized bed Fenton process.

2.2 Experimental apparatus

The gas-liquid fluidized bed reactor is composed of a plexiglass column with a diameter of 50mm and a height of 2000mm. It is equipped with a gas-liquid distributor at the bottom, and a round water bath surrounding the column. The gas-liquid distributor is connected to the gas compressor through a gas flow meter. A buffer tank is also included to prevent backflashing 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 2mm.

2.3 Experimental methods

The municipal landfill leachate samples were transferred to the fluidized bed Fenton process. COD value of the municipal landfill leachate sample was 2500mg/L. After the cylinder reached constant temperature, the oxidant was added, and the pH value in solution was adjust 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 diameters of 2mm. Samples were taken as predetermined intervals and were analyzed.

2.4 Analytical methods

COD values of samples were determined by using closed reflux method described in the standard methods [15].The value of pH was measured with a pH probe.

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 experimental condition for further research. Fig.1 depicts a typical 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 30min. After 30min, the decrease of residual organic compounds became insignificant. More foam was observed as the oxidation proceeded. This was evidence of carbon dioxide formation. The COD removal rate was about 61% at 30min. Based on the result, the reaction time for fluidized bed Fenton process was determined to be 30min for further experiments.

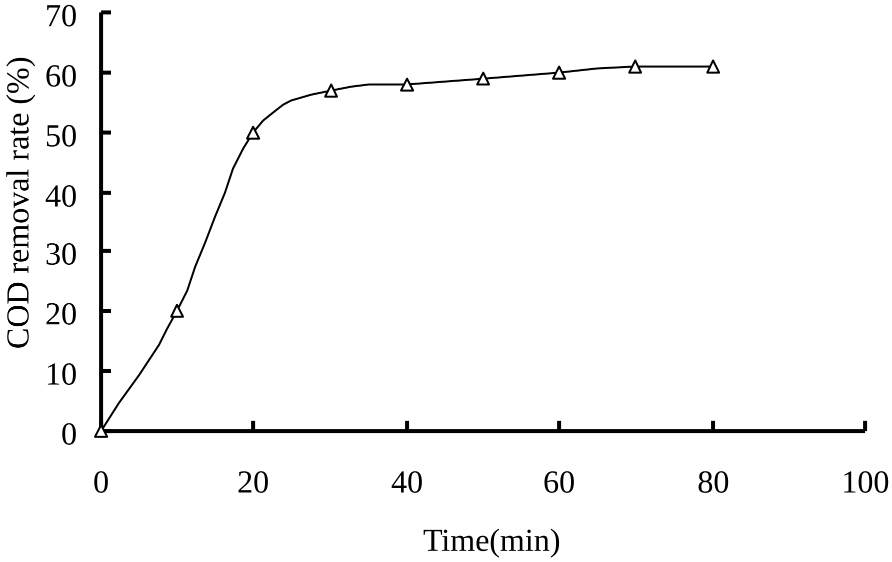

Fig.1 Effect of reaction time on COD removal rate. Experimental conditions: COD=2500mg/L, pH=3, $[H_2O_2]_0$=0.075mmol/L, $[Fe^{2+}]_0$=0.05mmol/L, ventilation volume of 0.12m^3/h, and temperature=333 K

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. pH affects the activity of both the oxidant and the substrate, the speciation of iron, and hydrogen peroxide decomposition. Sedlak and Andren explained higher hydroxyl radical product yields in the pH range of 2-4 by a reaction involving the organometallic complex where either hydrogen peroxide is regenerated or reaction rates are increased [16]. Fig.2 showed the effect of pH in solution on the COD removal rate. Either too high or too low pH value caused low COD removal rate. pH between 2.0 and 3.0 has been found effective, and best COD removal rate was obtained at pH 2.5.

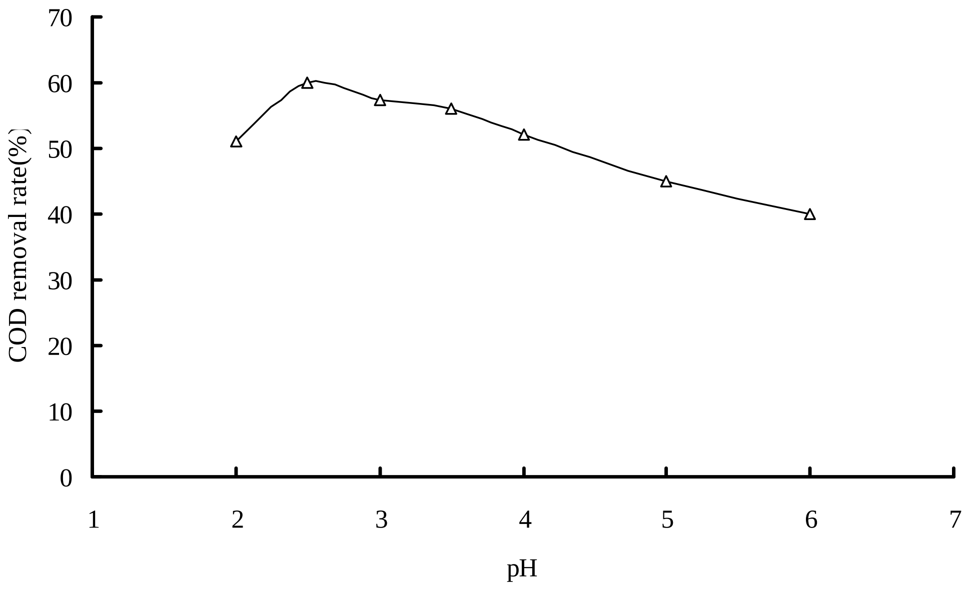

Fig.2 Effect of pH value on COD removal rate. Experimental conditions: COD=2500mg/L, reaction time of 30min, $[H_2O_2]_0$=0.075mmol/L, $[Fe^{2+}]_0$=0.05mmol/L, ventilation volume of 0.12 m^3/h, and temperature=333 K

At low pH, the reaction could be slowed down because hydrogen peroxide can stay stable probably solvating a proton to form an oxonium ion (e.g. $H_3O_2^+$). An oxonium ion makes hydrogen peroxide electrophilic to enhance its stability and presumably to reduce substantially the reactivity with ferrous ion. At the same time, the formed complex species $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ also react more slowly with hydrogen peroxide. In addition, the scavenging effect of the $HO^\bullet$ radical by H^+ is severe. On the other hand, at high pH, the oxidatio 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 $HO^{\bullet}$ radical[17].

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

In Fenton process, iron and hydrogen peroxide are two major chemicals determining operation costs as well as efficacy. Determination of the favorable amount of the Fenton's reagent is highly important. Fig.3 shows the effect of initial [Fe^{2+}] on the COD removal rate.

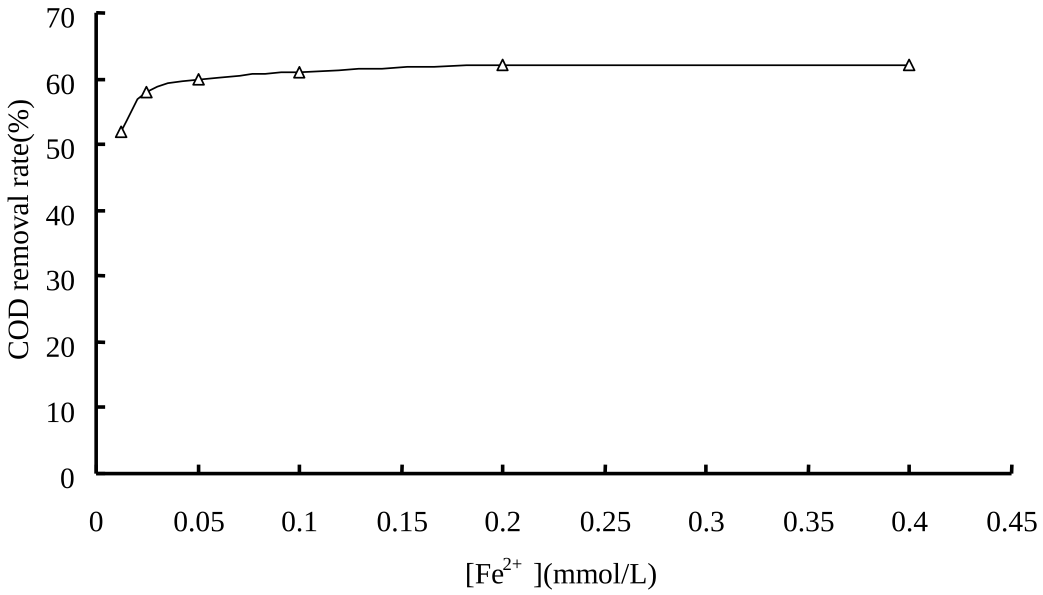

Fig.3 Effect of initial [Fe^{2+}] on COD removal rate. Experimental conditions: COD=2500mg/L, reaction time of 30min, pH=2.5, [H_2O_2]$_0$=0.075mmol/L, ventilation volume of 0.12 m^3/h, and temperature=333 K

From Fig.3, it can be seen that the COD removal rate increases with increasing initial [Fe^{2+}] concentration. It may be explained by the redox reactions since $HO^{\bullet}$ radicals may be scavenged by the reaction with the hydrogen peroxide or with another Fe^{2+} molecule as below. The lower COD removal rate capacity of Fe^{2+} at small concentration is probably due to the lowest $HO^{\bullet}$ radicals production abailable for oxidation[17].

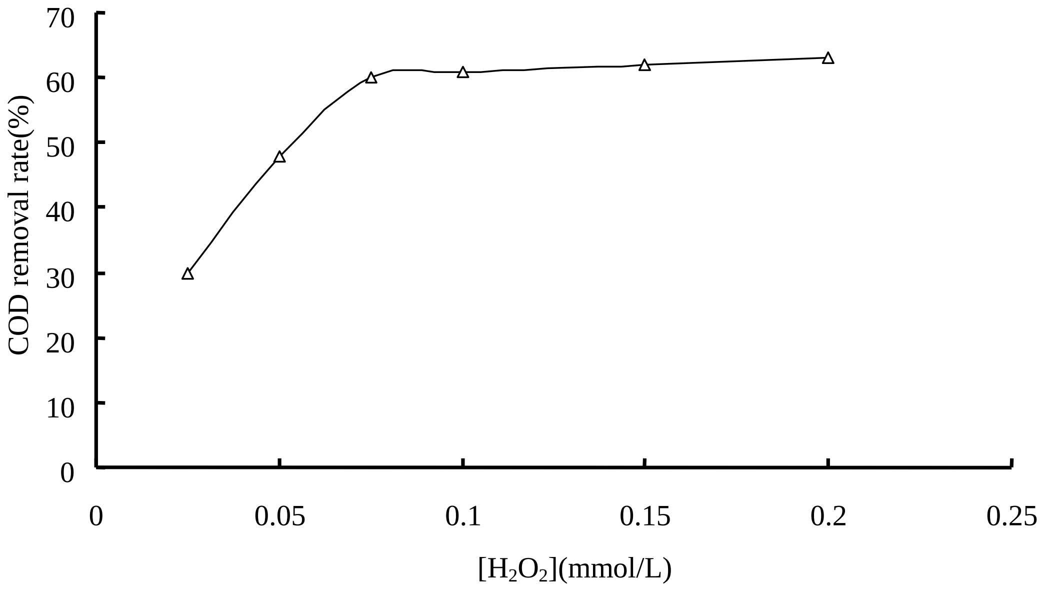

Fig.4 Effect of initial [H_2O_2] on COD removal rate. Experimental conditions: COD=2500mg/L, reaction time of 30min, pH=2.5, [Fe^{2+}]$_0$=0.05mmol/L, ventilation volume of 0.12m^3/h, and temperature=333 K

3.4 Effect of [H_2O_2] on COD removal rate
Fig.4 show the relationship between the COD removal rate and the initial concentration of H_2O_2.

As it can be seen, the effect of increasing the concentration of H_2O_2 from 0.025mmol/L to 0.075mmol/L was positive for the degradation of organic compounds from the municipal landfill leachate. This is due to the oxidation power of Fenton process which was imporved with increasing $HO^\bullet$ radical amount in solution obtained from the decomposition of increasing hydrogen peroxide. Further increase from 0.075mmol/L to 0.2mmol/L causes no significant change in COD removal rate. This may be explained by the fact that at a higher H_2O_2 concentration scavenging of $HO^\bullet$ radicals will occur, wich can be expressed by the Eqs.(1)[18]:

$$HO_2^\bullet + HO^\bullet \rightarrow H_2O + O_2 \quad (1)$$

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 the COD removal rate had a chage with the flow rate.

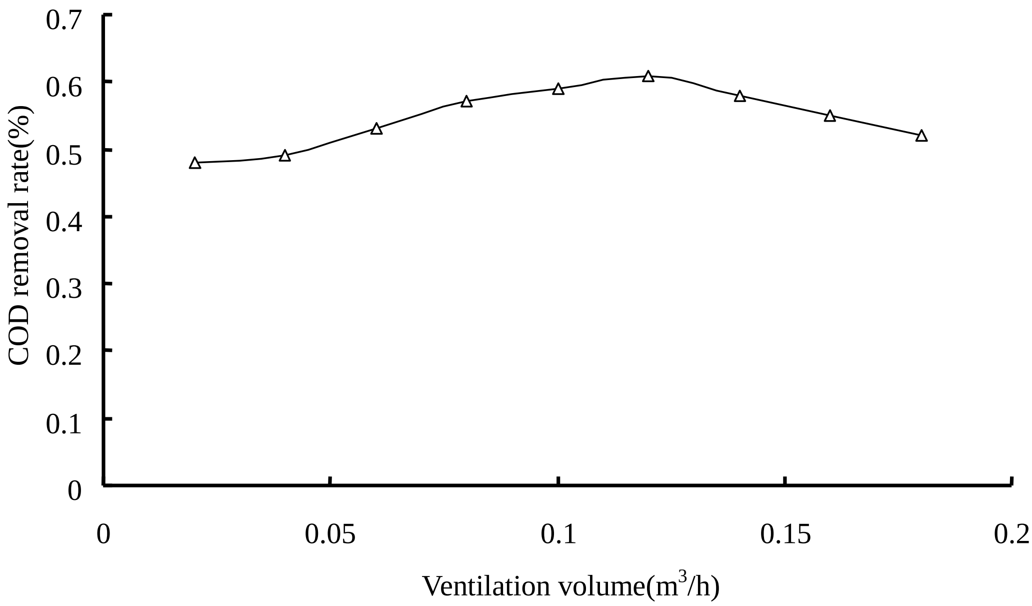

Fig.5 Effect of ventilation volume on COD removal rate. Experimental conditions: COD=2500mg/L, reaction time of 30min, pH=2.5, $[H_2O_2]_0$=0.075mmol/L, $[Fe^{2+}]_0$=0.05mmol/L, and temperature=333 K

When the gas flow rate was below 0.12m^3/h, the COD removal rate increased with the increasing flow rate However, when the gas flow rate was above 0.12m^3/h, the COD removal rate decreased. When the gas flow rate further increased, the fluidized bed was in a completed liquidized state, and heat and mass transfer were optimized. However, when the gasflow rate became too high, the tunnel effect reduced the mass transfer process, and consequently decreased the COD removal rate [19].

CONCLUSION

The effects of major parameters on the fluidized bed Fenton process were evaluated through treatment of the organic compounds from the manicipal landfill leachate. It was proved that the organic compounds from the municipal landfill leachate could be treated effectively using fluidized bed Fenton process. The optimal treatment condition was determined as: COD=2500mg/L, reaction time of 30min, pH=2.5, $[Fe^{2+}]_0$=0.05mmol/L, $[H_2O_2]_0$=0.075mmol/L, ventilation volume of 0.12m^3/h, and temperature=333 K. Under this condition, the maximum COD removal rate reached 61%.

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