Desalination and Water Treatment
www.deswater.com

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doi: 10.1080/19443994.2012.696415

47 (2012) 243–248
September

Taylor & Francis
Taylor & Francis Group

Treatment of landfill leachate by internal microelectrolysis and sequent Fenton process

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Received 12 October 2010; Accepted 27 February 2012

ABSTRACT

The treatment of landfill leachate was carried out in a bench scale reactor using internal microelectrolysis followed by Fenton process. The effect of operating conditions, such as reaction times of internal microelectrolysis and Fenton process, initial pH, cast iron dosage, and hydrogen peroxide concentration on COD removal, was investigated. The results showed that organic pollutants in the leachate were degraded swiftly during the first stage of both processes, but the increase of COD removal became insignificant with the progress of treatment. The optimal conditions were determined to be 3 of initial pH and 75 g/L of cast iron dosage. Under the optimal conditions, over 60% COD removal efficiency was achieved after 90 min of internal microelectrolysis and then 105 min of Fenton process with the addition of 195.6 mM hydrogen peroxide.

Keywords: Cast iron; Fenton reaction; Internal microelectrolysis; Landfill leachate

1. Introduction

It is well known that a landfill leachate contains nonbiodegradable and toxic organic compounds, and none of the biological treatments presented can effectively remove recalcitrant contaminants from the leachate [1]. As an alternative treatment method, advanced oxidation processes (AOPs) have been used for the pre-treatment and post-treatment of a landfill leachate [2–5]. Among a variety of AOPs, Fenton process is relatively inexpensive and is easy to operate and maintain [6–8]. The organic compounds (RH) in the leachate are oxidized by the hydroxyl radicals generated via Fenton reaction to produce highly reactive organic radicals ($R^{\cdot}$), which are further oxidized into smaller compounds [4,9],

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

$$RH + OH^{\cdot} \rightarrow H_2O + R^{\cdot} \rightarrow \text{furtheroxidation} \quad (2)$$

However, the conventional Fenton process may cause an additional pollution due to addition of the ferrous ions [10].

As a cost-effective treatment method, internal microelectrolysis is believed to operate on the principles similar to principle of electrolysis [11–13]. The difference between the internal microelectrolysis and electrolysis lies in the fact that the electrons are supplied due to the galvanic corrosion of many microscale sacrificial anodes rather than the external power supply [11,12]. It is well known that cast iron is an alloy of iron, carbon, and other elements. When cast iron is in contact with the leachate, several microscopic galvanic cells are formed between the

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iron (anode) and the carbon (cathode). The electrode reactions can be illustrated as follows:

$$\text{Anode (iron): } Fe(s) - 2e^- \rightarrow Fe^{2+}(aq) \tag{3}$$

Cathode (carbon):

$$\text{Acidic } 2H^+(aq) + 2e^- \rightarrow 2[H] \rightarrow H_2(g) \tag{4}$$

$$\text{Neutral to alkaline } O_2(g) + 2H_2O + 4e^- \rightarrow 4OH^-(aq) \tag{5}$$

The organics in the leachate are removed by oxidants generated during the internal microelectrolysis and through coagulation by iron hydroxides [11,12]. Moreover, when hydrogen peroxide is applied into the reaction system after internal microelectrolysis, it is decomposed to generate hydroxyl radicals by the ferrous ion via the reaction (1) or on metal surfaces [14],

$$M + H_2O_2 \rightarrow M^+ + OH^- + OH^\cdot \tag{6}$$

$$H_2O_2 + OH^\cdot \rightarrow H_2O + HO_2^\cdot \tag{7}$$

$$HO_2^\cdot \rightleftharpoons H^+ + O_2^{\cdot -} \tag{8}$$

$$M^+ + O_2^{\cdot -} \rightarrow M + O_2 \tag{9}$$

$$M + HO_2^\cdot \rightleftharpoons M^+ + HO_2^- \tag{10}$$

The generated hydroxyl radicals oxidize the organics in the leachate. Therefore, in this study, the internal microelectrolysis coupled with Fenton process was proposed for the treatment of landfill leachate. Batch experiments were carried out to investigate the performance of the combined internal microelectrolysis−Fenton process. The optimal conditions for COD removal from the landfill leachate were determined by evaluating the effects of operating conditions such as the reaction times of internal microelectrolysis and Fenton process, initial pH, cast iron dosage, and hydrogen peroxide concentration on the COD removal efficiency.

2. Materials and methods

The leachate samples were taken in polyethylene bottles from a sanitary landfill in Wuhan, China. The landfill was put into operation in 2003 with a designed storage capacity of 3.2×10^6 m^3 and currently receives about 800 tons of wastes per day. The samples taken were preserved in a refrigerator at 4℃ in accordance with the Standard Methods [15]. Its characteristics were pH 6.4, ammonia–nitrogen 1,300 mg/L, alkalinity as $CaCO_3$ 10,400 mg/L, and COD 8,546 mg/L (on average).

The cast iron filings were obtained from one factory of the Wuhan University and degreased with ethanol for about 20 min. They were stored for use in a beaker containing dilute sulfuric acid to prevent the oxidation of previously cleaned and unoxidized cast iron after the residual ethanol was evaporated. Sodium hydroxide was of chemically pure (CP) grade and all other chemicals used were of analytical reagent (AR) grade. All solutions were prepared using distilled water.

The solution pH was measured with an Orion $420A^+$ pH meter. The COD was determined by using a microwave-assisted potassium dichromate method adapted from Jardim and Rohwedder [16].

The batch experiments were performed without repetition in a reactor containing 200 mL leachate and a selected amount of cast iron (Fig. 1). The initial pH value was adjusted with concentrated sulfuric acid and sodium hydroxide solution. The mixing was provided by a mechanical stirrer (Model 78-1, Hangzhou Instrument Motors Factory, China). The Hydrogen peroxide was applied all at once after internal microelectrolysis. At pre-selected time intervals, the samples were taken with a syringe and filtered into the tubes containing sodium hydroxide solution to quench the reaction by increasing the pH to around 8.0. Then, they were diluted and settled for 30-min. The supernatant was taken for the COD analysis.

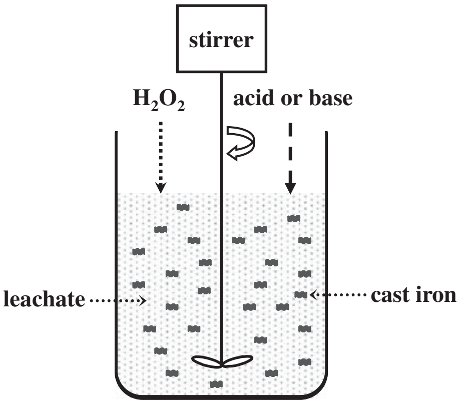

Fig. 1. The schematic diagram of an experimental setup.

3. Results and discussion

3.1. Effect of internal microelectrolysis time

The effect of reaction time on the internal microelectrolysis process was investigated when the initial pH was 3 and the cast iron loading was 75 g/L, respectively. As can be seen in Fig. 2, the COD was quickly removed from the leachate during the first stage of internal microelectrolysis and 38.6% COD removal was achieved after a 90-min treatment. The increase in COD removal became insignificant afterwards, and a slight COD was removed when the time reached 120-min. This is in agreement with the result by Yang when polyester wastewater was treated by internal microelectrolysis [17]. With the progress of internal microelectrolysis, more and more ferrous and ferric hydroxides were generated. The hydroxides precipitate on the cast iron surface and block the electron transfer between iron and wastewater [11]. This resulted in deactivation of the cast iron surface and termination of internal microelectrolysis.

Based on the results, the reaction time for the internal microelectrolysis followed by Fenton reaction was determined to be 90-min for further experiments.

3.2. Effect of Fenton reaction time

Fenton reaction was initiated when hydrogen peroxide was applied into the reactor after a 90-min internal microelectrolysis. As illustrated in Fig. 2, the COD removal was significant at the beginning of Fenton process and the total COD removal reached 62.7% after a 105-min Fenton treatment. However, further extension of Fenton reaction time led to slight COD removal. This is similar to the report by Lopez et al. [20]. They observed that the Fenton oxidation of landfill leachate was over after two hours, and about 60% of the initial COD value (i.e. 10,540 mg/L) was removed at 10,000 mg/L of hydrogen peroxide dosage. When hydrogen peroxide was introduced into the reaction system, it is catalyzed by the elemental iron (reaction 6) and ferrous ion (reaction 1) to generate the hydroxyl radicals. Then, the leachate is swiftly degraded by the hydroxyls radicals (reaction 2) when a large amount of iron-active surface sites and ferrous ions are available. However, the regeneration of ferrous ion via the produced ferric ion by the following reaction is much slower [18],

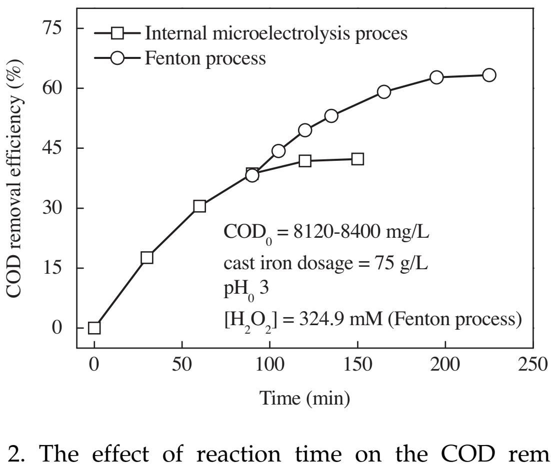

Fig. 2. The effect of reaction time on the COD removal efficiency during internal microelectrolysis and Fenton processes.

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^{\cdot} \tag{11}$$

and the ferric ion has a lower catalytic activity than the ferrous ion [19]. Moreover, the iron-active surface sites are blocked by degradation products. As a result, Fenton reaction slows down. On the other hand, the hardly oxidizable products, such as carboxylic acids, are formed with the progress of Fenton process [19,20], and consequently the increase of COD removal becomes insignificant during the last stage of the Fenton process. As can be seen in Fig. 2, the total COD removal efficiency after 135 min Fenton treatment was only 63.3% compared with 62.7% COD removal efficiency at 105 min.

Based on the results, the reaction time for Fenton process following the internal microelectrolysis was determined to be 105 min for further experiments.

3.3. Effect of initial pH

The initial pH values investigated were 1, 3, 5 and 7, respectively, when the cast iron dosage was 75 g/L and the hydrogen peroxide concentration was 324.9 mM. Fig. 3 indicates that acid condition favored the COD removal. The total COD removal was only 18.9% when the initial pH rose to 7. However, too low initial pH (pH_0 1) also leads to a decrease in COD removal.

It was a normally held view that it is necessary to conduct an internal microelectrolysis under acid conditions (pH 2–3) to obtain a high removal efficiency [13]. The increase in pH results in the precipitation of both ferrous ion and ferric ion, which blocks the electron transfer between the iron and the leachate [11]. This accounted for the deactivation of the cast iron surface and the termination of internal microelectrolysis. On the other hand, less amount of ferrous ion was present in the leachate on account of ferrous ion precipitation. Furthermore, Deng and Englehardt were of the opinion that the optimal pH

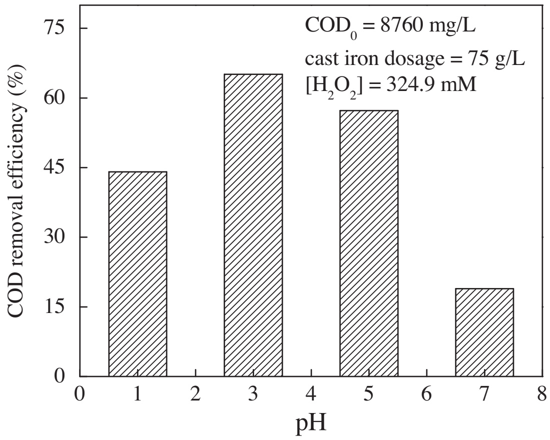

Fig. 3. The effect of initial pH on the COD removal efficiency.

values for the Fenton treatment of landfill leachate range between 2.0 and 4.5 [3]. As a result, the sequent Fenton reaction is also inhibited at a pH above 3. But when the pH dropped to 1, the scavenging effect of the hydroxyl radicals by hydrogen ions becomes pronounced [21–23],

$$^{\cdot}OH + H^+ + e^- \rightarrow H_2O \tag{12}$$

Moreover, the regeneration of ferrous ion via reaction (11) is inhibited, and the formed $[Fe(H_2O)]^{2+}$ catalyzes the hydrogen peroxide slowly [3]. Consequently, less hydroxyl radicals are generated to degrade the landfill leachate. As can be observed in Fig. 3, only 44.1% COD was removed at pH_0 1, while the highest COD removal efficiency (65.1%) was achieved at pH_0 3. Wu et al. also observed that a less COD removal was obtained at pH_0 1 than at pH_0 3 [24].

Therefore, the selection of a pH condition for further experiments was pH_0 3 based on the COD removal efficiencies.

3.4. Effect of cast iron dosage

Fig. 4 illustrates the COD removal at different the cast iron dosages when hydrogen peroxide concentration was 324.9 mM and initial pH was 3. Generally, the number of microscopic galvanic cells increased proportionally to the cast iron dosage [12]. In addition, the generation of hydroxyl radicals through the decomposition by elemental iron and ferrous ion is improved with cast iron dosage. As expected, the COD removal efficiency increased almost linearly with an increase in the cast iron dosage up to 75 g/L. However, when the cast iron dosage exceeded 75 g/L, the generated ferrous ionswere also excessive and scavenge the hydroxyl radicals,

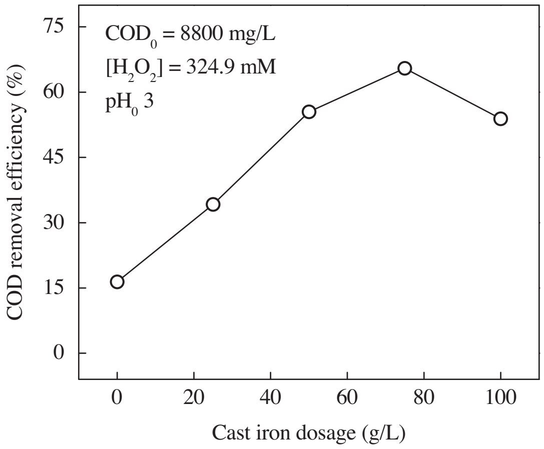

Fig. 4. The effect of cast iron dosage on the COD removal efficiency.

$$Fe^{2+} + OH^{\cdot} \rightarrow Fe^{3+} + OH^- \tag{13}$$

Therefore, any further increase in the cast iron dosage results in the decrease of COD removal. Fig. 4 shows that 53.9% COD was obtained at 100 g/L of cast iron dosage compared with the highest COD removal of 65.5% at 75 g/L of cast iron dosage. In a similar integrated process (i.e., internal microelectrolysis in combination with ozonation) for the degradation of reactive red X-3B aqueous solution, Ruan et al. observed that the COD removal rate increased with the increase of cast iron dosage, but an excessive dosage of the cast iron results in the decrease of the COD removal rate [12].

Based on the results, the optimal cast iron dosage was determined to be 75 g/L for further experiments.

3.5. Effect of hydrogen peroxide concentration

Hydrogen peroxide concentration is one of the major factors that significantly influences Fenton process and determines the operation cost. The effect of hydrogen peroxide concentration on the COD removal efficiency was investigated when the cast iron dosage was 75 g/L and the initial pH was 3. As shown in Fig. 5, the presence of hydrogen peroxide significantly enhances the COD removal. However, the effect of hydrogen peroxide concentration was less pronounced than that of cast iron dosage. This was due to the fact that cast iron influenced the Fenton process as well as the internal electrolysis. However, Fenton reaction was initiated only after hydrogen peroxide was applied. With the increase in hydrogen peroxide, the scavenging effect of hydrogen peroxide on hydroxyl radicals becomes significant [3,5],

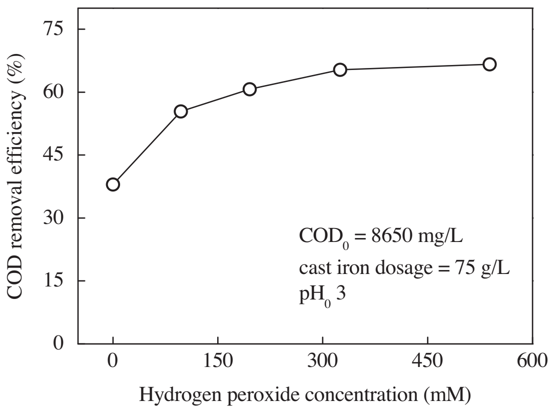

Fig. 5. The effect of hydrogen peroxide concentration on the COD removal efficiency.

$$^{\cdot}OH + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \qquad (14)$$

As observed in Fig. 5, the COD removal efficiency increased from 55.4 to 60.7% when the hydrogen peroxide concentration rose from 97.0 to 195.6 mM. However, as the hydrogen peroxide concentration continued to increase from 324.9 to 538.8 mM, the COD removal increased by only 1.3% compared with the 65.3% COD removal at 324.9 mM. In Fenton process, it was observed that the addition of an overdose of hydrogen peroxide could not improve the COD removal from the landfill leachate [5,7,24]. Supposing the prices of both hydrogen peroxide and cast iron are RMB 1,000 per 1,000 kg and 1 kg COD needs to be removed from the leachate, the operation costs would be RMB 18.2, 18.9, and 20.4 when COD removal efficiencies are 55.4, 60.7, and 65.3%, respectively. Therefore, the selection of hydrogen peroxide should balance the COD removal efficiency and the operation cost, and then a 195.6 mM hydrogen peroxide dosage was chosen, so that over 60% COD removal efficiency would be obtained at an operation cost of RMB 18.9 per kg COD removal.

4. Conclusion

The landfill leachate could be efficiently treated by the combined internal microelectrolysis–Fenton process. The addition of hydrogen peroxide at the end of internal microelectrolysis would improve COD removal significantly. The favorable durations for microelectrolysis and Fenton process were 90 and 105 min, respectively. The experimental results showed that the treatment conditions, such as initial pH, cast iron dosage, and hydrogen peroxide, had a significant influence on the COD removal. The optimal conditions were determined to be 3 of initial pH and 75 g/L of cast iron dosage, and a 60.7% of COD removal efficiency was achieved at an operation cost of RMB 18.9 per kg COD removal when 195.6 mM hydrogen peroxide was applied into the reaction system.

Acknowledgments

This study was supported by the Wuhan Science and Technology Bureau, China (Grant No. 201060723313) and the National High-Tech R&D Program (863 Program) of China (Grant No. 2008AA06Z332). We appreciate the valuable comments of the anonymous reviewers.

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