Photoelectrochemical treatment of landfill leachate in a continuous flow reactor

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ARTICLE INFO

Article history:

Received 23 May 2009

Received in revised form 25 August 2009

Accepted 25 August 2009

Available online 30 September 2009

Keywords:

Landfill leachate

Photoelectrochemical treatment

Flow reactor

Electrolysis

UV light irradiation

ABSTRACT

Leachate from a municipal landfill site, which has been treated by biological process, was treated by photoelectrochemical oxidation in a pilot scale flow reactor, using DSA anode and UV light irradiation. At a current density of 67.1 mA/cm² and 2.5 h reaction time, the removal rates achieved were for 74.1% COD, 41.6% for TOC, and 94.5% for ammonium in the electrolysis process with UV light irradiation. In comparison, the removal rates of COD, TOC, and ammonium were decreased in the individual electrolysis process, respectively. The increase induced by the UV light irradiation was analyzed. The removal rates increased with the increase of current densities in the photoelectrochemical process. Combined with UV–vis spectra and gas chromatography–mass spectroscopy analysis, it is believed that the organic contaminants were efficiently mineralized into small molecular acids. At the meantime, the concentrations of metal ions in the landfill leachate were largely reduced.

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1. Introduction

Sanitary landfills are the primary method currently used for municipal solid waste disposal in many countries, and leachate generated from landfills is a high-strength wastewater exhibiting acute and chronic toxicity (Fan et al., 2008; Renou et al., 2008; Salem et al., 2008). Untreated leachates can permeate groundwater or mix with surface water and contribute to the pollution of soil, groundwater, and surface water (Salem et al., 2008). Biological methods are very effective for the treatment of landfill leachate with a high value of biological oxygen demand (BOD) but are ineffective if recalcitrant compounds are present, so that a physical–chemical process is required (Lei et al., 2007). Great attention has been directed toward either new chemical and physical processes or traditional methods (Rivas et al., 2005; Primo et al., 2008). O₃, O₃/H₂O₂, and O₃/UV have been used in treating landfill leachate recently (Wu et al., 2004). The Fenton reaction (Deng and Englehardt, 2006) and heterogeneous photocatalysis have also been proved to be an alternative as a tertiary treatment (Cho et al., 2002). Generally, the above advanced oxidation processes depends on hydroxyl radicals' reaction. Landfill leachate had high concentration of alkalinity that can react with hydroxyl radicals with high reaction rate. Therefore, alkalinity need to be removed by pH adjustment before these reactions (Cho et al., 2004).

Electrochemical technology offers an efficient means of controlling pollution and it has become available in the last two decades.

Application of electrochemical methods in treating landfill leachate has been investigated (Cossu et al., 1998; Moraes and Bertazzoli, 2005; Cabeza et al., 2007; Anglada et al., 2009). Generally, high concentration of Cl[−] was present in the landfill leachate. In the electrolysis of landfill leachate, indirect oxidation induced by the active chloride radicals will occur, which are not dependant on the hydroxyl radicals. Thus, the organic contaminants and NH₃–N will be removed in the electrolysis process (Chiang et al., 1995a).

Recently, photoelectrochemical (PEC) oxidation has been proven an efficient method in removing organic contaminants than individual electrolysis and photocatalysis process. It has been reported that the landfill leachate can be efficiently removed by photo-assisted electrolysis method (Taichert et al., 2006). In that work, the PEC treatment permits almost total decolonization and typical COD removal of about 60% within 300 min. And, the static PEC process was carried out in a glass reactor with 1 L of capacity, equipped with water refrigeration and magnetic stirring. The cathode and anode were titanium grid and DSA commercial, respectively. In the current work, a pilot scale flow electrochemical reactor was used for landfill leachate treatment with the assistance of UV light irradiation. In comparison with the electrolysis process, an obvious increase in the removal of NH₃–N, COD, TOC, and BOD were observed in the PEC process. The enhanced mechanism was analyzed; effects of current densities and reaction time were investigated.

2. Methods

PEC process was carried out in a reactor with 6.5 L capacity. The tubular DSA anode was concentrically located at the center of the

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Fig. 1. Photoelectrochemical reaction system used in the current study.

reactor. The dimension and length of the tubular DSA anode was 60 mm and 1125 mm, respectively. The stainless steel outside of the reactor was also used as the cathode. A UV lamp (20 W, main wavelength 254 nm) in a quartz glass tube was located at the center of the reactor. The system was submitted to various current densities controlled by a DC-stabilized power with a maximum output of 300 A and 10 V. The setup is described in Fig. 1.

Leachate samples with biological treatment were collected from a sanitary landfill located in the city of Beijing and stored at a temperature of 4 °C for a maximum of 10 days in order to maintain their characteristics. In Table 1, the initial characteristics of the landfill leachate is presented. After biological treatment, the COD_{Cr}, TOC, and NH₃-N are still high. And, the chlorine concentration is as high as 4500 mg/L.

The experiment was operated in a continuous flow mode. During the experiments, leachate samples were periodically collected for analysis. No reactants or supporting electrolyte were added to the leachate prior to the experiments. The progress of electrochemical oxidation was monitored by measuring COD and TOC. The concentrations of COD were determined with a COD analyzer (HATO[®] CTL-12, China). The TOC was determined with multi N/C 3000 TOC analyzer (Analytik Jena AG Co., Germany) after the solution was filtered through a 0.45 µm filter. UV-vis spectra of the samples were recorded on a U-3010 UV-vis spectrophotometer (Hitachi Co., Japan). The values of pH were measured using an Orion 720APLUS Benchtop meter (Thermo Orion Co., USA). For gas chromatography-mass spectroscopy (GC-MS) analysis, the residue was trimethylsilylated with 0.2 mL of anhydrous pyridine, 0.1 mL of hexamethyldisilazane, and 0.05 mL of chlorotrimethylsilane at room temperature. GC-MS analysis was carried out on an Agilent 6890GC/5973MSD with a DB-5 MS capillary column. The concentration of metal ions in the landfill leachates was examined via an ICP-OES (SCIEX Perkin Elmer Elan mode 5000). Before the mea-

surement, the pH values of landfill leachates were adjusted to 2.0 in order to dissolve the metal oxides.

3. Results and discussion

3.1. Degradation characteristics of landfill leachate in EC and PEC process

As shown in Fig. 2A, in individual EC process, within 2.5 h, ammonium was efficiently removed, 47.5% COD and 28.3% TOC were removed, respectively. By contrast, in PEC process, nearly 74.1% COD and 41.6% TOC were removed. These results indicated that UV light irradiation increased the removal rate of COD and TOC in the leachate efficiently. As shown in Fig. 2B, all the values of BOD₅/COD in EC and PEC processes were increased with the evolution of reaction time. Furthermore, it can be seen from Fig. 2B that the increased value of BOD₅/COD in PEC process is larger than that in the individual EC process, which confirmed the advantage of PEC process. At the meantime, nearly no reduction of COD, TOC, and BOD₅ in the individual photolysis process was observed (data not shown).

In EC process, oxidant species such as hydroxyl radicals will form on the anode surface. On the other hand, chloride ions usually

Fig. 2. (A) Degradation characteristic of landfill leachate in EC and PEC process with the current density of 67.1 mA/cm² and reaction time of 2.5 h; (B) changes of BOD₅/COD with the time in EC and PEC processes with current densities of 67.1 mA/cm² and reaction time of 2.5 h.

Table 1
Characteristics of the landfill leachate.

Parameter	Content
pH	7.80
Conductivity (mS cm ⁻¹)	14.74
Alkalinity (CaCO ₃)	6300
TDS ^a	8150
COD	560
TOC	190
NH ₃ -N	700
Chlorine	4500

^a Average values. Units in mg/L.

Fig. 3. Variation of active Cl^- amount with the time in EC and PEC processes with the current densities of 67.1 mA/cm^2 and reaction time of 2.5 h.

present in landfill leachates are oxidized to chlorine/hypochlorite. All of these oxidation species are responsible for the oxidation of organic pollutants and ammonium removal.

In PEC process, COD reduction efficiency ranges from 70% to above 90%, and ammonium removal efficiency almost reaches

100% under appropriate conditions. Chiang et al. (1995b) found that removal of ammonium was obviously dominant when in competition with removal of COD under indirect oxidation during electro-oxidation of an old leachate. Cossu et al. (1998) reported that the removal rate of ammonium was lower than that of COD at the initial stage of electro-oxidation of an old leachate when direct oxidation predominated, and then ammonium was substantially removed in the subsequent electro-oxidation stage when indirect oxidation became prevalent. Our results are consistent with the above conclusions. The variation of active Cl^- amount in the reaction solution was examined in PEC and EC processes, respectively. It can be seen from Fig. 3 that more active Cl^- radicals were produced in PEC process than that in EC process, which may be responsible for the more efficient removal of COD in PEC process than that in EC process.

3.2. Effect of applied current densities on PEC degradation of landfill leachate

Current density, the current per unit area of electrode, may be the most frequently referred term in an electrochemical process because it controls the reaction rate. It can be seen from Fig. 4 that nearly no removal of ammonium and COD was observed at the current density of 29.0 mA/cm^2 . With the increase of current density, ammonium and COD were obviously removed; the removal rate

Fig. 4. Effect of current densities on PEC degradation of landfill leachate. (A) $\text{NH}_3\text{-N}$; (B) COD removal; (C) TOC removal; (D) BOD_5/COD .

increased with the current density. A possible explanation is that an increased current density during electro-oxidation enhanced chlorine generation, which was probably responsible for subsequent removal of ammonium. Chiang et al. (1995b) reported that during electro-oxidation of leachate with the current density of 25.00 mA/cm², COD removal efficiency was about 50% higher than that by electro-oxidation with 6.25 mA/cm². In our case the Cl⁻ concentration was high as 4500 mg/L. Thus, the indirect oxidation plays a predominant role in the removal of COD and ammonium.

During the electrochemical oxidation of landfill leachate, pollutant removal may be primarily due to indirect oxidation, utilizing chlorine/hypochlorite formed by anodic oxidation of chlorine originally existing or added in the leachate, although direct anodic oxidation may to some extent destroy pollutants adsorbed on the anode surface. Hypochlorite generated is a strong oxidant that can oxidize aqueous organic compounds. Chiang et al. (1995b) found that COD and ammonium removal efficiencies in electro-oxidation of leachate increased with the current density. However, in a direct electrochemical oxidation, pollutant removal efficiency at the same charge loading (in coulomb per litre) is independent of current density. Hence, Chiang et al. (1995a) suggested that indirect oxidation was the main process during electrochemical oxidation of leachate. Moreover, they proposed that ammonium removal can be due to a series of reactions between hypochlorite and ammonia.

3.3. Analysis of organic contaminants in landfill leachate in PEC process

It can be seen from Fig. 5 that the solution pH decreases with the extension of reaction time under various current densities. In PEC reaction, the ammonium was removed and some organic pollutants with large molecular weight were degraded into some organic acids or small molecular acids, which are responsible for the decrease of solution pH. The UV-vis spectra variation with the reaction time was shown in Fig. 6. It is shown that the intensity increase at the initial 30 min and decrease subsequently when the wavelength was less than 300 nm. When the wavelength was larger than 300 nm, the wavelength decrease throughout the reaction time. These results indicate that some intermediates produced at the initial reaction time, which were subsequently degraded with the reaction evolution. As shown in Supplementary material of Fig. 1, the organic pollutants in the leachate are largely reduced after PEC reaction for 2.5 h.

Fig. 5. Variation of solution pH in PEC reaction with various current densities.

Fig. 6. Variation of solution UV-vis spectra of landfill leachate with the reaction time in the photoelectrocatalytic process (applied current density of 67.1 mA/cm²).

Table 2

The concentration variation of metal ions in the landfill leachate.

Metal ions	Raw water	After PEC treatment without pH adjustment	After PEC treatment with pH adjustment
Fe	8.96	9.46	1.95
Cu	4.18	6.83	0.94
Zn	17.75	21.24	2.04
Pb	0.07	0.10	UD
Cd	0.012	0.01	UD
Cr	2.06	0.96	0.19
Mn	1.46	1.85	0.02

Current density of 67.1 mA/cm²; reaction time of 2.5 h; UD, undetected.

At the meantime, the metal ions in the landfill leachate before and after PEC treatment were analyzed (Table 2). It is shown that the concentrations of nearly all metal ions increased after PEC treatment. It is measured that the pH value was decreased to 2.0 after PEC process. In this case, many metal oxides or complexes will dissolve into metal ions, which are responsible for the concentration increase of metal ions. Furthermore, the pH was adjusted from 2.0 to 6.0. It is seen that the concentration of all metals ions decreased largely.

In PEC degradation of landfill leachate, some chlorinated byproducts will be generated by the indirect oxidation effect of chlorine/hypochlorite. However, the undesired byproducts can be removed after PEC reaction for a relatively long time (Chiang et al., 2002). Meanwhile, their studies indicate that chlorination of humic acid conducted by electrochemical oxidation process produces less absorbable halogenated compounds than the chlorination conducted by HOCl oxidation. Therefore, PEC process can be concluded to be environmentally friendly for the treatment of landfill leachate than the individual electro-oxidation process.

4. Conclusions

The results have shown that PEC treatment is a more promising process for the degradation and remediation of effluents of low biodegradability in landfill leachate than single electrolysis method. At a current density of 67.1 mA/cm² and 2.5 h reaction time, the removal rates achieved were for 74.1% COD, 41.6% for TOC, and 94.5% for ammonium in the electrolysis process with UV light irradiation. In comparison, the removal rates of COD, TOC, and ammonium were decreased in the individual electrolysis process,

respectively. PEC oxidation of landfill leachate under appropriate conditions can remove most COD and almost all ammonia, and also significantly remove color. Reduction of pollutants appears to be primarily due to indirect oxidation. The ammonia was removed and organic contaminants were degraded into small molecular acids. And, the total metal ions concentrations of Fe, Cu, Zn, Pb, Cd, Cr, and Mn decreased after PEC reaction with the pH adjustment.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos. 50538090, 20977103, 50778172, 20837001). This research was also supported by the Knowledge Innovation Program of the Chinese Academy of Sciences (RCEES-QN-2007Z007) and the Special Funds for Young Scholars of RCEES, CAS.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.biortech.2009.08.098](https://doi.org/10.1016/j.biortech.2009.08.098).

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