Pretreatment of concentrated leachate by the combination of coagulation and catalytic ozonation with Ce/AC catalyst

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ABSTRACT

A raw concentrated leachate produced from membrane bioreactor-nanofiltration (MBR-NF) was taken from Chengdu Chang’an Waste Landfill Site, China. The major fraction of this concentrated leachate was large refractory humic substances. A coagulation–ozonation process was applied to treat this leachate, aiming at enhancing chemical oxygen demand (COD) removal efficiency and increasing its biodegradability. Meanwhile the molecular size distribution of the leachate, before and after coagulation and ozonation treatment, was analyzed by using ultrafiltration membrane separation. Coagulation pretreatment effectively removed varieties of large molecules in the raw concentrated leachate. The addition of Ce/AC greatly improved the oxidative ability of O₃ in COD removal in the ozonation of coagulated leachate. The biochemical oxygen demand (BOD₅)/COD ratio increased from 0.011 for the untreated concentrated leachate to 0.30 for the effluent of the coagulation–catalytic ozonation process, which indicated that a subsequent biological treatment could be readily conducted. The stability test demonstrated that the Ce/AC catalyst was effective and stable in the catalytic ozonation process. According to the results of molecular size distribution analysis, a direct correlation was observed between the increase of BOD₅/COD and the decrease of apparent molecular weight.

Key words | activated carbon, advanced oxidation processes, catalytic ozonation, cerium oxide, concentrated leachate, landfill leachate

INTRODUCTION

Landfill leachate is a complex wastewater generated from sanitary landfilling which is nowadays the most commonly used method to eliminate municipal solid wastes. The composition of landfill leachate varies depending on the nature of the waste deposited and the age of the landfill (Chen 1996; Park et al. 2001). Biological processes such as activated sludge process, sequencing batch reactors and membrane bioreactors (MBRs) are usually used to treat landfill leachate owing to their low cost and effective results. After a biological stage, further treatments such as coagulation–flocculation, ultrafiltration (UF), evaporation, incineration, nanofiltration (NF) and reverse osmosis (RO) have been employed worldwide (Renou et al. 2008). In China, an MBR-NF combined process is adopted to treat landfill leachate to achieve a satisfactory removal of refractory pollutants (Su et al. 2007; Dong et al. 2013). This combined process has high treatment efficiency, low energy consumption and operational flexibility (Su et al. 2007). However, the further treatment of the concentrated leachate produced from membrane treatment depends on its environmental, technical and economical sustainability (Calabro et al. 2010).

Concentrated leachate, representing typically 13–30% of total incoming landfill leachate (Van der Bruggen et al. 2003b; Liu et al. 2008), is characterized by high concentrations of salts and high content of non-biodegradable humic substances (Zhang et al. 2009, 2013). Although the landfill recirculation of concentrated leachate has a negligible effect on its qualitative and quantitative characteristics in the period immediately after reinjection begins (Peters 1998a, b), it is not sustainable in the long term due to its negative effects on leachate production (Calabro et al. 2010). Removing contaminants is one of the sustainable
possibilities to treat concentrated leachate (Van der Bruggen et al. 2005a). A pre-treatment before biological treatment is essential because of its high chemical oxygen demand (COD) and low ratio of biochemical oxygen demand (BOD) of COD (Calabro et al. 2010).

Pre-treatment approaches, such as activated carbon adsorption (Kurniawan & Lo 2009; Cataldo & Angelini 2013), Fenton treatment (Singh & Tang 2013; Singh et al. 2013), electrochemical processing (Xiao et al. 2013), H₂O₂ oxidation (Qureshi et al. 2002), and ozone-based advanced oxidation processes (Wang et al. 2004a, b; Wu et al. 2004; Tizaoui et al. 2007; Van Aken et al. 2011) have been extensively investigated in the treatment of leachate or concentrated leachate. Catalytic ozonation, one of ozone-based advanced oxidation processes, is an effective method for treatment of high concentrated, toxic and biorefractory wastewater. Ozonation cleaved molecular weight intermediates (Wang et al. 2004a, b). More- over, a reduction in COD of about 45% and an increase in biodegradability (BOD₅/COD) from 0.1 to 0.34 were observed in heterogeneous catalytic ozonation of landfill leachate using activated carbon and perlite as catalysts (Tizaoui et al. 2007).

In previous works, Ce/AC was proved to be a promising ozonation catalyst in the degradation of commercial fulvic acids (Qin et al. 2014) and humic substances extracted from concentrated leachate (Qin et al. 2015). Ce/AC was expected to be a good catalyst in the treatment of landfill leachate by ozone. The aim of this work was to study the possibility of removing COD and enhancing biodegradability of the concentrated leachate produced from MBR-NF treatment by a coagulation-catalytic ozonation process. The effect of Ce/AC catalyst on color removal, COD removal and molecular size distribution are discussed. The biodegradability improvement of concentrated leachate was evaluated by the ratio of BOD₅/COD.

**EXPERIMENTAL**

**Materials**

The concentrated leachate was obtained from Chengdu Chang’an Waste Landfill Site, PR China. The characteristics of landfill leachate might vary dramatically with time. Therefore, the concentrated leachates (L₁, L₂ and L₃) were collected in February 2012, May 2013 and March 2014, respectively. All coagulation and ozonation experiments in this study were conducted using concentrated leachate sample L₃. Humic acids (HA), fulvic acids (FA) and non-humic substance (NHS) were extracted from the concentrated leachate based on methods described by Thurman & Malcolm (1984). The wastewater was filtered with two sheets of medium speed qualitative filter paper to remove suspended particles before coagulating.

A commercial activated carbon from Xinsen Carbon Industry Co., Ltd (Pingluo, China) was used. The AC samples were crushed and sieved to 40–80 mesh, washed several times with deionized water, and then dried at 110 °C for 24 h. The CeO₂/AC catalyst was prepared by incipient wetness impregnation. Activated carbon samples were impregnated with aqueous solution of Ce(NO₃)₃·6H₂O to obtain a nominal Ce loading of 5 wt.%. The resultant samples were dried at 110 °C for 24 h and then calcined in a tube furnace under a flow of N₂ + H₂ (N₂ 40 cm³ min⁻¹ and H₂ 10 cm³ min⁻¹, measured at room T and P) at 450 °C for 3 h, with a heating rate of 3 °C min⁻¹. All other chemicals required in the experiments were analytical grade reagents. The textual characterization of AC and CeO₂/AC catalyst samples was determined with a Builder SSA-4200 apparatus using N₂ as the adsorbate at 77 K. The textural properties such as surface area, pore volume, pore size were determined by nitrogen adsorption. Nitrogen adsorption and desorption isotherms were recorded on a nitrogen adsorption system.

**Coagulation tests**

The coagulation process was performed in a 2 L beaker. One thousand millilitres filtered leachate samples were coagulated, achieving final ferric chloride (FeCl₃) concentrations of 600–1600 mg L⁻¹. The pH of the initial samples was varied between 4.0 and 9.0. The samples were stirred at a rapid mixing of 250 rpm for 2 min while the coagulant was added, and then at a slow mixing of 60 rpm for 20 min. After this time, the stirring was stopped and the sample was left to settle for 30 min. The color and COD of the filtered sample was measured. The optimum ferric chloride dosage and pH value were determined.

**Ozonation procedure**

The ozonation experiments were carried out in a 2 L glass reactor equipped with agitation and a circulation jacket. In each experiment, the reactor was filled with 1.5 L coagulated leachate. Ozone was produced from pure oxygen (200 cm³ min⁻¹) by a laboratory ozone generator (Jinan Sankang Co., Ltd, China) and bubbled into an ozonation
reactor through a sintered metal filter at the reactor bottom. In the adsorption and catalytic ozonation experiments, 750 mg of catalyst was introduced into the reactor. In the adsorption experiments, the ozone-containing stream was replaced by an oxygen stream. The experiments were performed at constant inlet ozone concentration (42 mg L$^{-1}$). The stirring rate was maintained at 270 rpm and the temperature was set to 20 °C. Samples were periodically withdrawn and immediately filtered with a 0.45 μm membrane for further analysis. The residual ozone was quenched by the addition of Na$_2$S$_2$O$_3$ solution. The excess ozone in the outlet gas was absorbed by 2% KI solution and then decomposed by activated carbon column.

The stability test of the catalyst was performed in a bubbling bed reactor (length 400 mm, ID 20 mm) equipped with a circulation jacket. In the catalytic ozonation experiments, 50 mL catalyst particles (10–16 mush) were packed under a layer of ceramic rings. Ozone (200 mL min$^{-1}$) was bubbled into ozonation reactor through a porous glass plate at the bottom of the reactor. The coagulated leachate (2 mL min$^{-1}$) was fed into the ozonation reactor by means of a pump (Shanghai Tauto Biotech Co., Ltd, China). The reaction temperature was set to 20 ± 1 °C. The excess ozone in the outlet gas was absorbed by 2% KI solution and then decomposed by activated carbon column.

**Analytical methods**

Ozone concentrations in the gas and aqueous solution were measured by iodometric titration method (Rankess et al. 1996) and indigo method (Bader & Hoigné 1981), respectively. The leachate was characterized by color, COD and BOD$_5$. COD and BOD$_5$ were analyzed following the standard methods for examination of water and wastewater of China: HJ/T 399-2007 and HJ/T 86-2002, respectively. COD was analyzed by sealed catalytic digestion-colorimetric methods using a DR1010 COD tester (Hach, America). BOD$_5$ was determined by the speedy testing method of microorganism sensor with BOD-220A tester (SIPO, Tianjin, China). To determine the distribution of apparent molecular weight (AMW) before and after coagulation and ozonation, an ultrafiltration membrane separation was employed. Concentrated leachate samples were filtered with 0.45 μm membrane filters and molecular sieves of 1 K, 5 K, 10 K and 30 K Dalton. The pH in the system was monitored by a pH5-5 pH meter (Chengdu Fangzhou Technology Co., Ltd, China).

Since the visible region of the leachate spectrum showed no limited absorption maxima, Krüll & Dopkens (2004) proposed the use of the color number CN to quantify the color of landfill leachate. And CN can be calculated using:

$$CN = \frac{SAC_{436}^2 + SAC_{525}^2 + SAC_{620}^2}{SAC_{436} + SAC_{525} + SAC_{620}}$$  \hspace{0.5cm} (1)

$$SCA_x = \frac{Abs_x}{\chi}$$  \hspace{0.5cm} (2)

where SAC is the spectral absorption coefficient in the visible range at wavelengths of 436, 525 and 620 nm; Abs$_x$ is the absorbance at the corresponding wavelength; and $\chi$ is the cell thickness.

**RESULTS AND DISCUSSION**

**Characteristics of concentrated leachate**

The characteristics of concentrated leachate samples (L$_1$, L$_2$ and L$_3$) are summarized in Table 1. The pH values of three concentrated leachate samples were neutral or weakly alkaline. The values of COD were 3500, 3280 and 3136 mg L$^{-1}$ for sample L$_1$, L$_2$ and L$_3$ respectively. The results were higher than another report (Zhang et al. 2015). The corresponding values of BOD$_5$/COD were 0.020, 0.011 and 0.016, respectively, indicating the low biodegradability of the concentrated leachate. This was mainly attributed to the fact that readily biodegradable fractions could be decomposed into CO$_2$, H$_2$O and small molecular weight substances in MBR process. While high-molecular-weight and non-biodegradable compounds such as HA and FA were mostly removed by membrane processes and accumulated in the concentrated leachate (Chan et al. 2007).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>L$_1$</th>
<th>L$_2$</th>
<th>L$_3$</th>
<th>Mean</th>
<th>Discharged limit$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.1</td>
<td>7.8</td>
<td>7.8</td>
<td>7.8</td>
<td>6.0–9.0</td>
</tr>
<tr>
<td>COD (mg L$^{-1}$)</td>
<td>3500</td>
<td>3280</td>
<td>3136</td>
<td>3305</td>
<td>100</td>
</tr>
<tr>
<td>BOD$_5$ (mg L$^{-1}$)</td>
<td>69</td>
<td>35</td>
<td>50</td>
<td>51</td>
<td>–</td>
</tr>
<tr>
<td>BOD$_5$/COD</td>
<td>0.020</td>
<td>0.011</td>
<td>0.016</td>
<td>0.016</td>
<td>–</td>
</tr>
<tr>
<td>HA (COD, mg L$^{-1}$)</td>
<td>856</td>
<td>823</td>
<td>801</td>
<td>827</td>
<td>–</td>
</tr>
<tr>
<td>FA (COD, mg L$^{-1}$)</td>
<td>1671</td>
<td>1391</td>
<td>1425</td>
<td>1496</td>
<td>–</td>
</tr>
<tr>
<td>NHS (COD, mg L$^{-1}$)</td>
<td>973</td>
<td>1066</td>
<td>910</td>
<td>983</td>
<td>–</td>
</tr>
</tbody>
</table>

HA and FA, main organic pollutions in concentrated leachate, might increase the difficulty of the treatment of leachate, since HA and FA could not be easily oxidized and biodegraded. In this study, the average percentage of HA, FA and NHS in concentrated leachate were about 25.0%, 45.3% and 29.7%, respectively. The humic substance (HA and FA) content of concentrated leachate (70.0%) was slightly less than the result reported by Zhang et al. (HA 40.9% and FA 34.1%) (Zhang et al. 2009), but higher than the result of raw landfill leachate reported by Fan et al. (HA 22% and FA 26%) (Fan et al. 2007). Moreover, FA predominated in the concentrated leachate. A similar observation was reported by Nanny & Ratasuk (2002). FA could transform into HA as landfilling age increased.

The effect of initial pH on COD removal and CN was also determined. Figure 1(b) presents the COD removal and CN at different pH. The initial pH varied from 4 to 9 at a coagulant dosage of 1400 mg L^{-1}. The variation in initial pH was significant in COD removal from concentrated leachate. The optimum pH to attain a better removal percentage of 32.4% was 6, which was inconsistent with the results reported by Wang et al. (2002).

Thus, the optimum dosage of ferric chloride and pH was 1400 mg L^{-1} and 6, respectively. After the coagulation, the COD removal rate of concentrated leachate (R_{COD}) was 32.5% and the COD was reduced to about 2120 mg L^{-1} (see Table 2). The color removal was about 88% and the CN was reduced to about 0.29.

Coagulation by ferric chloride

As is shown in Figure 1, the dosage of coagulant and pH were determined as a function of COD removal and CN. For the purpose of determining the optimum dosage of coagulant, the ferric chloride concentration was varied from 600 to 1600 mg L^{-1} while the coagulation process was run at the unadjusted pH of 7.8. Figure 1(a) shows the effect of ferric chloride dose on COD removal and CN in the coagulation process. It presents that the highest removal percentage for COD was 24.5% obtained at the ferric chloride concentration of 1400 mg L^{-1}. The COD removal and CN reduction were increased with increasing coagulant dosage up to the optimum dosage and then they decreased as the coagulant dosage was further raised.

Catalytic ozonation of coagulated leachate with CeO2/AC

Color removal

Figure 2 shows the color removal in the single and catalytic ozonation processes. The color reduction was nearly 100% for ozonation alone and catalytic ozonation. The color removal efficiency depended on the characteristics of the color-causing compounds and the treatment method (Wang et al. 2003). The chromophores of humic substances include quinoid structures and azo structures which were very vulnerable to the attack of molecular ozone (Wang et al. 2004a, b). Therefore, the addition of catalysts did not much improve color removal.
COD removal and biodegradability enhancement

In the previous papers, CeO₂/AC presented high catalytic activity in ozonation of humic substances, so it was expected to be an effective catalyst in ozonation of landfill leachate. The COD removal of coagulated leachate in the single and catalytic ozonation is presented in Figure 3. Compared to the removal of color, COD removal was difficult, since the COD removal efficiency was only about 27.1% in the single ozonation. In the catalytic ozonation, the COD removal efficiencies were 36.9% and 43.8% for AC, and Ce/AC, respectively. The COD removal for catalytic ozonation with Ce/AC was about 17% higher than that of ozonation alone. The enhancement of COD removal following the addition of catalysts could be explained by the powerful oxidation effect of ·OH radicals resulting from ozone decomposition in the presence of AC and Ce/AC catalyst (Lin et al. 2002; Rivera-Utrilla & Sanchez-Polo 2004; Valdes & Zaror 2006). It can be seen from Table 2 that the COD removal efficiency of concentrated leachate reached 62% by the combination of coagulation and catalytic ozonation with Ce/AC.

Another objective of the ozonation process is to enhance its biodegradability. Thus, the biodegradable organic pollutants can be removed in a subsequent biological process that is much cheaper than oxidation processes. The biodegradability of leachate can be described in terms of BOD₅/COD ratio. Table 2 presents the BOD and BOD₅/COD ratio in different ozonation processes. After ozonation, the increase in BOD₅ and decrease in COD led to an increase in the BOD₅/COD ratio. It was found that coagulation–O₃ process improved biodegradability values from 0.011 (untreated concentrated leachate) to about 0.21. Furthermore, the addition of AC and Ce/AC catalysts showed a little improvement in biodegradability as compared to ozonation alone.

Specific ozone consumption

Specific ozone consumption, the ratio of mass of consumed ozone to mass of COD reduced, is an important parameter to estimate the operating costs. The ozone utilization efficiency \( \eta_{O_3} \) was calculated according to Equation (3):

\[
\eta(O_3) = \frac{m_T - m_{O_3} - m_R}{(COD_0 - COD) \cdot V}
\]

Table 2 | Effect of catalysts and reaction conditions on COD removal and the BOD/COD ratio of the ozonation effluents

<table>
<thead>
<tr>
<th>Processes</th>
<th>( R_{COD} ) (%)</th>
<th>( \eta(O_3) ) (mg ( O_3 ) mg COD⁻¹)</th>
<th>COD (mg L⁻¹)</th>
<th>BOD₅ (mg L⁻¹)</th>
<th>BOD₅/COD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coagulation</td>
<td>32.5</td>
<td>–</td>
<td>2120</td>
<td>248</td>
<td>0.12</td>
</tr>
<tr>
<td>Coagulation–O₃</td>
<td>50.8</td>
<td>1.67</td>
<td>1544</td>
<td>318</td>
<td>0.21</td>
</tr>
<tr>
<td>Coagulation–AC/O₃</td>
<td>57.4</td>
<td>1.25</td>
<td>1336</td>
<td>343</td>
<td>0.26</td>
</tr>
<tr>
<td>Coagulation–Ce/AC/O₃</td>
<td>62.0</td>
<td>1.14</td>
<td>1192</td>
<td>358</td>
<td>0.30</td>
</tr>
</tbody>
</table>
where $m_T$ is the mass of total applied ozone; $m_O$ is the mass of offgas ozone and it is determined by iodometric titration method because the excess ozone in the outlet gas is absorbed by 2% KI solution along the whole experiment; $m_R$ is the mass of residual ozone in the liquid phase and it is calculated by using the ozone concentration in the aqueous solution at the end of the experiment and the volume of coagulated leachate. COD_0 and COD are the initial and residual COD of coagulated leachate, respectively; $V$ is the volume of coagulated leachate.

As shown in Table 2, the single ozonation process presented the highest value for ozone consumption. Ozone consumption value decreased from 1.67 to 1.25 mg O₃ mg COD⁻¹ when AC was used and it reduced to 1.14 mg O₃ mg COD⁻¹ in the presence of Ce/AC, indicating that the addition of catalyst could lead to extensive COD removal together with reduced ozone consumption.

In previous work (Faria et al. 2009; Li et al. 2009; Orge et al. 2011), the degradation of organic compounds in catalytic ozonation with Ce/AC involved the hydroxyl radical mechanism. Some pollutants which were not vulnerable to the attack of molecular ozone could be decomposed by the non-selective hydroxyl radical and thus the specific ozone consumption decreased.

### Stability of Ce/AC catalyst

In order to investigate the stability of Ce/AC catalyst, the test was conducted in a fixed bed reactor. The COD removal efficiency and the biodegradability improvement of coagulated leachate were evaluated at different reaction times. The test process was performed for about 100 h.

As is depicted in Figure 4, from starting time to a reaction time of 5 h, the adsorption of organic compounds resulted in a rapid decrease of COD removal. As the adsorption capability of AC catalyst decreased, COD removal decreased slowly and finally reached a relatively constant value at about 8 h. The COD removal efficiency of coagulated leachate keeps to a nearly constant rate after a reaction time of 10 h. The stable COD removal efficiency was nearly 34%. Table 3 illustrates that the surface area of the spent Ce/AC catalyst after 60 h reaction is 957 m² g⁻¹, which is a little lower than that of new Ce/AC catalyst sample (1376 m² g⁻¹). Moreover, it is seen from Table 3 that the decrease of total pore volume ($V_T$) is mainly due to the reduction of the mesoporous volume. In terms of biodegradability, it was found that the BOD₅/COD value was nearly constant (0.23–0.25), indicating that the Ce/AC catalyst exhibited a high stability during the catalytic ozonation of coagulated leachate.

### Molecular size distribution analysis

The distribution of apparent molecular weight (AMW) of concentrated leachate obtained before and after coagulation and ozonation was analyzed depending on COD and the results are shown in Figure 5. The portions of COD in each range of AMW were calculated in comparison with the corresponding values. Figure 5(a) shows that the COD distribution of untreated leachate is 13.1% for AMW greater than 30 kDa, 20.92% for AMW between 10 k and 30 kDa, 24.74% for AMW between 5 k and 10 kDa, 22.70% for AMW between 1 k and 5 kDa and 18.62% for AMW less than 1 kDa. After applying the coagulation process, a significant change in the distribution of AMW was observed from 13.1% to 4.53% for the molecular weight range greater than 30 kDa (see Figure 5(b)), indicating that the coagulation mechanism would result in a substantial removal of larger organic molecules (Wu et al. 2004).
It was noted that after ozonation alone (Figure 5(c)), the organic pollutants of AMW greater than 30 kDa disappeared and the predominant COD distribution would be significantly shifted to the AMW less than 1 kDa (65.28%), which demonstrated that the pollutants with larger molecular weight had been oxidized into smaller ones. Furthermore, as shown in Figure 5(d), Ce/AC/O₃ produces much greater destruction of the large organic compounds into small pieces with the 74.5% portion in COD distribution less than 1 kDa. These results are thought to have a direct relationship with the increase of biodegradability of concentrated leachate.

CONCLUSIONS

The combination of ferric chloride coagulation and catalytic ozonation with Ce/AC was studied for the treatment of concentrated leachate. The following conclusions were drawn from the results of this research:

1. Ferric chloride coagulation could effectively remove larger organic molecules in the raw concentrated leachate, showing a COD removal efficiency of 32.5% and a color removal rate of 88%.
2. In the ozonation of coagulated leachate, the addition of Ce/AC catalyst greatly improved the oxidative efficiency of O₃ for COD removal, thus the COD removal efficiency was about 17% higher than that of ozonation alone. Moreover, ozone consumption value decreased from 1.67 to 1.14 mg O₃ mg COD⁻¹ when Ce/AC catalyst was used.
3. The BOD₅/COD ratio increased from 0.011 for the raw concentrated leachate to 0.30 for the effluent of the catalytic ozonation process, indicating biodegradability enhancement. Leachate separated by ultrafiltration membrane indicated that the composition shifted from larger molecules into smaller ones. A subsequent biological treatment could be readily conducted.
4. The stability test demonstrated that the Ce/AC catalyst was effective and stable in the catalytic ozonation coagulated leachate. A combination of coagulation and
catalytic ozonation may be a promising approach to concentrated leachate treatment.

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