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Calcium and organic matter removal by carbonation process with waste incineration flue gas towards improvement of leachate biotreatment performance

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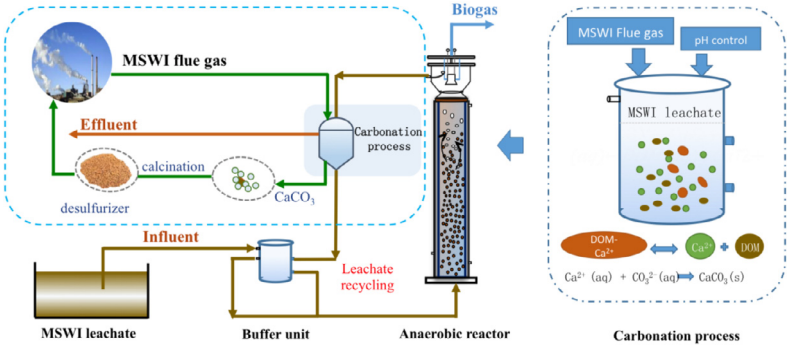
HIGHLIGHTS

- Waste incineration flue gas was used to remove calcium from MSWI leachate.
- Calcium removal was 95–97% with 100 min of carbonation at pH of 10.0–11.0.
- 10–16% of COD removal was obtained during the carbonation.
- NH_4^+-N and TP decreased by 19.7–37.7% and 72.5–83.5%, respectively.
- Optimal Ca removal was 91.5% with 60–80 min of carbonation at pH of 11.0.

GRAPHICAL ABSTRACT



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ABSTRACT

Municipal solid wastes incineration (MSWI) flue gas was employed as the carbon source for in-situ calcium removal from MSWI leachate. Calcium removal efficiency was 95–97% with pH of 10.0–11.0 over 100 min of flue gas aeration, with both bound Ca and free Ca being removed effectively. The fluorescence intensity of tryptophan, protein-like and humic acid-like compounds increased after carbonation process. The decrease of bound Ca with the increase of precipitate indicated that calcium was mainly converted to calcium carbonate precipitate. It suggested that the interaction between dissolved organic matter and Ca^{2+} was weakened. Moreover, 10–16% of chemical oxygen demand removal and the decrease of ultraviolet absorption at 254 nm indicated that some organics, especially aromatic compound decreased via adsorption onto the surface of calcium carbonate. The results indicate that introduce of waste incineration flue gas could be a feasible way for calcium removal from leachate.

1. Introduction

Municipal solid wastes incineration (MSWI) leachate is characterized by a complex mixture of various organic compounds with weak acidity. It usually has higher chemical oxygen demand (COD range of 40,000–60,000 mg/L), metals (e.g., calcium 3000–6000 mg/L) and ammonia nitrogen (NH_4^+-N: 1000–2000 mg/L) than landfill or compost leachate (Dang et al., 2013; Lei et al., 2016; Ye et al., 2011). Compared with other reactors, expanded granular sludge bed (EGSB) reactors achieved efficient performances, with higher organic loading rate (OLR) more than 40 kg COD/m^3·d and 90–96% COD removal efficiency when treating fresh landfill leachate (Liu et al., 2010; Luo et al., 2014a,b) and incineration leachate (Dang et al., 2013).

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In the anaerobic reactors, calcium, as an important factor, has been studied a lot. Usually, appropriate calcium (150–300 mg/L) is found to be benefit for the metabolic activity of sludge and improve the settle ability via granulation enhancement (Langerak et al., 1998; Xia et al., 2016). However, high calcium concentration in leachate often lead to fouling problems on the inner walls of the EGSB bioreactor and along the effluent tubes (Liu et al., 2011; Lu et al., 2016). The large amount of calcium precipitate (e.g. $CaCO_3$ or $Ca_3(PO_4)_2$) blocks the sludge bed at the bottom of the reactor, seriously affecting the reactor operation (Langerak et al., 2000; Liu et al., 2011, 2010). At the same time, due to the high calcium precipitate on the sludge granules, the activity of the microorganism is lowered, thereby affecting the biological treatment performance (Yu et al., 2001). The methane production reduces with calcium concentration of 1600–1800 mg/L (Liu et al., 2011), and the specific methanogenic activity is inhibited when calcium ion is more than 2000 mg/L (Dang et al., 2014; Ye et al., 2011). Therefore, measures must be taken to effectively remove calcium from calcium-rich MSWI leachate to improve the efficiency of anaerobic biological treatment in a long-term run.

CO_2 stripping is the most feasible and economic method to remove calcium from leachate rather than using ion exchange method or scale inhibitor. Luo et al. (2014a) and Lu et al. (2016) investigated the feasibility of biogas recirculation for calcium removal of 92.8–96.5% in an EGSB reactor treating compost leachate. It suggested that CO_2 in waste gas mixture could serve as the carbon source to remove calcium in leachate. In MSWI flue gas, CO_2 almost accounts for 10%–15% (Jiang et al., 2013). Moreover, MSWI flue gas is usually with temperature of about 100–200 °C, and more than 70 °C at the exit of a spray tower. This high temperature flue gas could further elevate the temperature of MSWI leachate and reduce energy consumption during anaerobic treatment. Therefore, it could be a promising carbon source for calcium removal from MSWI leachate.

Calcium in leachate can be fractionated into three forms using ion exchange and size fractionation: particulate and colloidal matter >0.45 μm, free cations/labile complexes <0.45 μm, and non-labile complexes <0.45 μm (Oygard et al., 2007). Calcium in non-labile complexes cannot easily dissociate because of the interaction of Ca^{2+} with acidic groups (e.g. carboxyl and hydroxyl) in humic-like substances (Ahn et al., 2008; Wang et al., 2006). Organics in this form are less susceptible to be removed and metals here can be deemed to have a low bioavailability (Oygard et al., 2007). Moreover, the re-flocculation of protein with Ca^{2+} might also slow down the degradation of protein (Li et al., 2014). Thus, a clear distinction could be made between various forms of calcium and organic matter in the carbonation process.

In this work, aeration time of MSWI flue gas and pH were studied to obtain the optimal carbonation conditions. Additionally, calcium ion morphology analysis together with size fraction were investigated to figure out the transformation behavior of calcium and organic matters in leachate. Moreover, possible effects on anaerobic biological treatment were taken into account with further analyses of COD, ultraviolet absorption at 254 nm (UV_{254}), fluorescence excitation-emission matrix (EEM) spectroscopy, together with total phosphorus (TP) and NH_4^+-N. It would provide a better understanding towards the carbonation process of MSWI leachate using MSWI flue gas.

2. Materials and methods

2.1. Leachate

The leachate used in this study was obtained from a municipal solid waste incineration plant in Shanghai, China. The characteristics of the leachate are similar to previous used MSWI leachate (Luo et al., 2014b), with pH of 3.8–5.6 and COD concentration of 55,272–56,274 mg/L. Ammonia nitrogen (924 mg/L), total phosphorus (91 mg P/L) and Ca concentration (3784 mg/L) were also monitored.

2.2. Carbonation process

The MSWI flue gas (CO_2 volume fraction: 4%; flow: 24–27 L/min) from the spray tower was pumped into the MSWI leachate for 2 h using sodium hydroxide to adjust pH to pH = 9.0, pH = 10.0 and pH = 11.0, respectively. The working volume was 15 L in each batch. Samples were taken out every 30 min and filtered with a 0.45 μm cellulose membrane for further analysis.

2.3. Fractionation

Size fractionation of the leachate was carried out using an ultrafiltration cell device (300 mL) with a 0.45 μm cellulose membrane and polysulfone membranes of 100 kDa (kilodalton), 50 kDa, 10 kDa and 1 kDa (Wang et al., 2006). This process was driven by high purity nitrogen with pressures of 0.05 MPa–0.22 MPa.

2.4. Calcium ion morphology analysis

Cationic exchange resin was used to separate free cations/labile complexes <0.45 μm, and non-labile complexes <0.45 μm (Ca from these two part were defined as: free Ca and bound Ca, respectively) (Oygard et al., 2007). Pretreatment of cationic resin: first washed the cationic resin (Sodium type 732 cation resin, Sinopharm) with distilled water. Then they were cleaned using 5% HCl and NaOH solution in turn with constant stirring and end up with 5% HCl to remove any contamination. Finally washed with distilled water to neutral pH. Leachate samples after filtration were adjusted to alkalescency, then they were added to resin column and eluted with ultrapure water. The eluting solution was then sampled for detection of bound Ca. The concentration of free Ca was obtained by the difference between the total calcium and the bound Ca. Pre-experimental was conducted with the same batch of leachate samples for several times, with similar results being achieved. Thus, the experiments in this study were conducted only once and using the same batch of experimental data for analysis.

2.5. Sampling and analytical methods

All chemicals used in this study were of analytical grade. All samples were taken out and filtered using 0.45 μm Millipore filters at different time intervals. COD, TP and NH_4^+-N were measured according to Standard Methods (APHA, 2012). The pH was detected using PHS-3C meter.

Calcium and other metals content was determined using an atomic emission spectrometry system equipped with inductively coupled plasma (ICP-AES, Optima 2000 DV, Perkin-Elmer) after full digestion by HNO_3–HCl–$HClO_4$ in a 120 °C graphite furnace.

EEM fluorescence was determined by an F79 Pro fluorescence spectrophotometer (LENGGUAGN, China). Samples were diluted until TOC < 10 mg/L (total organic carbon). The excitation wavelengths were from 200 to 600 nm with 5 nm steps and the emission wavelengths were detected from 250 to 650 nm with 1 nm steps, using MATLAB for data processing analysis. The recorded EEMs were corrected first by subtracting the water background. The fluorescence intensity was calculated by integrating the peak area (Dong et al., 2010). The UV–Vis absorption was measured at 254 nm using a 4802 UV/VIS spectrophotometer (Unico, China).

X-ray diffraction (XRD) patterns of the precipitates were collected in D\max-2550X diffractometer (Japan) operated at 40 kV