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Calcium effect on anaerobic biological treatment of fresh leachate with extreme high calcium concentration

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ABSTRACT

Fresh leachate from municipal solid waste (MSW) incineration plant in China always contains extremely high concentration of calcium which would reduce the bioactivity of microorganisms and lead to calcium precipitation in granules. This paper investigated the effect of high concentration of calcium on anaerobic granular sludge without calcium precipitation by static tests for 72 h, and on anaerobic bio-treatment process for treating fresh leachate in a laboratory-scale expanded granular sludge bed (EGSB) reactor with calcium precipitation for 132 d. The results showed that, suppression thresholds of calcium concentration for anaerobic granular sludge were 5000 mg/L from both static tests and EGSB reactor operation. Calcium precipitation in anaerobic granules was a gradual formation process, mainly in the form of calcium carbonate calcite. Compared with calcium precipitation, high calcium concentration was mainly responsible for the decrease of COD removal efficiency in treatment process. Only a few microorganisms survived when calcium concentration increased over 5000 mg/L, which was mainly concentrated in *Clostridium* of bacteria and *Methanosaeta* of archaea.

1. Introduction

Municipal solid waste (MSW) incineration develops rapidly all over the world in recent years due to its advantages in MSW disposal and energy production (Chou et al., 2009). In developing countries, huge amount of fresh leachate from incineration plants generates during the waste storage period (for 3–7 d) before incineration, because of the low calorific value and high moisture of MSW (Nie, 2008). This leachate needs to be treated individually as wastewater instead of spraying back to the incinerator furnaces which is commonly used in many European countries (Chen and Christensen, 2010). In the past decade, it has been frequently proved that anaerobic treatment was the most cost-effective technology for the treatment of fresh landfill leachate (Agdag and Sponza, 2005; Calli et al., 2006; Parawira et al., 2006; Kheradmand et al., 2010). However, the treatment of fresh leachate from MSW incineration plants, the water quality of which is different from fresh landfill leachate (Chen and Christensen, 2010), are rarely reported.

Compared with landfill leachate, high calcium concentration (sometimes > 5000 mg/L) is one of the most typical characteristics for leachate from MSW incineration plant, especially in developing countries (Nie, 2008; Ye et al., 2011). This is mainly due to the large amount of kitchen garbage without classification. Calcium in leachate may lead to calcium precipitation in granular sludge and scaling on the bioreactor wall and along effluent pipes, which would affect the operation of the reactor, and even cause accidents in the actual projects (Van Langerak et al., 1998; Kim et al., 2003, 2004). Furthermore, high concentration of calcium would also influence the bio-treatment efficiency due to the calcium precipitation on granular sludge and the decrease of the biological activity of the microorganism (Yu et al., 2001; Liu et al., 2011). So far, there is no cost-effective way for high calcium wastewater pretreatment in real project. And the high calcium wastewater, for example, fresh leachate is usually directly transported into the bio-treatment unit. Therefore, it is important to investigate the calcium effect on wastewater treatment processes.

It has been reported that the calcium precipitation on sludge would reduce the biomass activity (Yu et al., 2001). And the channels in cell membrane for calcium ions transferring into microbial cells are different from those for sodium and potassium ions ("calcium channel" at Dorland's Medical Dictionary, http://www.dorlands.com). Thus, the presence of high calcium concentration in fresh leachate from MSW incineration plant cannot simply equal to salinity caused by sodium and potassium. To the best of our knowledge, studies on anaerobic bio-treatment of high calcium

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wastewater generally stayed at relatively low concentrations of calcium (about 1000 mg/L) for actual wastewaters (Van Langerak et al., 1998; Yu et al., 2001; Fernández-Nava et al., 2008), or high calcium concentration for static tests or simulated wastewaters (Ahn et al., 2006). The suppression threshold of calcium concentration for bio-treatment of fresh leachate from MSW incineration plant needs to be evaluated. Meanwhile, the effects of calcium concentration and calcium precipitation on biomass activity of anaerobic granular sludge are still unclear.

This paper investigated the suppression threshold of calcium concentration and impact of calcium precipitation for anaerobic granular sludge treating fresh leachate from MSW incineration plant. Two set of experiments (static tests for 72 h and expanded granular sludge bed (EGSB) reactor for 132 d) were carried out to demonstrate the effect of calcium concentration and calcium precipitation. Calcium precipitation was characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). The microbial communities in granular sludge samples throughout the operation process of EGSB reactor were analyzed by denaturing gradient gel electrophoresis (DGGE).

2. Materials and methods

2.1. Fresh leachate

The fresh leachate used as the feed in this study was obtained from an MSW-to-energy incineration plant in Beijing, China. The characteristics of the leachate were shown in Table 1. Raw leachate was diluted with tap water as influent, and then stored at 4 °C in a refrigerator.

2.2. Laboratory-scale EGSB reactor treating fresh leachate

The suppression threshold of calcium concentration together with impact of calcium precipitation for anaerobic granular sludge treating fresh leachate from MSW incineration plant was investigated in a laboratory-scale EGSB reactor. The reactor, the schematic of which was shown in the previous study by Dang et al. (2013) with working volume of 4.5 L, was operated stably at 33 ± 1 °C throughout the study. Internal recirculation was applied and the liquid up-flow velocity was maintained at 2.0 m/h. The anaerobic granular sludge inoculated into the EGSB reactor was 6.6 g VSS/L (volatile suspended solids), taken from a full-scale UASB reactor using to treat brewery wastewater in Henan, China, with VSS/TSS (total suspended solids) of 0.72. The hydraulic retention time (HRT) was kept at 2.5 d, and the sludge retention time (SRT) was between 32 d and 49 d.

The fresh leachate was diluted with tap water as feed of the EGSB reactor. In order to avoid the influence of organic load and high concentration free ammonia, we diluted the leachate till the COD of which was about 17,000 mg/L so as to ensure the COD and ammonia concentrations (free ammonia concentration was in the range of 23–32 mg/L in the reactor) were lower than the suppression threshold mentioned in other studies (Ye et al., 2011; Liu et al., 2012). After anaerobic sludge acclimated to the diluted leachate composition (operating for 1.5–2 SRT), keep the leachate concentration in influent and gradually increase the calcium concentration by adding calcium chloride to investigate the calcium effect on the treatment process in EGSB reactor. Wang et al. (1995) reported that no inhibition effect on the anaerobic system occurred when the accumulated Cl^- concentration was less than 20,000 mg/L.

Table 1
Characteristics of the leachate from the MSW incineration plant (unit: mg/L, except for pH).

Item	Value	Item	Value
COD	70,390–75,480	Ca	3275–5827
BOD_5	39,250–46,458	Na	2273–3728
NH_4^+–N	1042–1395	Mg	463–1598
TN	1330–2179	Fe	59.1–679.9
TP	104.6–163.8	Mn	4.56–43.50
Cl^-	3978–4729	Zn	13.9–36.5
SO_4^{2-}	1833–2907	Pb	1.11–7.61
pH	4.58–6.42	Ni	0.91–2.3

2.3. Static tests

The suppression threshold of calcium concentration for anaerobic granular sludge in static tests was measured by specific methanogenic activity (SMA). The sludge was withdrawn from the EGSB reactor treating fresh leachate at the end of start-up period (without calcium precipitation). Take the same weight of sludge into a series of 125-mL serum bottles with media (acetic acid 15,000 mg COD/L, NH_4Cl 1700 mg/L, KH_2PO_4 370 mg/L, $MgSO_4$ 90 mg/L, trace elements 0.1 mL, Na_2S solution 1000 mg/L yeast extract 2000 mg/L, pH 7, Ahn et al., 2006) and different concentrations of calcium (0 mg/L, 500 mg/L, 1000 mg/L, 2000 mg/L, 3000 mg/L, 5000 mg/L, 8000 mg/L) under strict anaerobic conditions and incubate them in water bath shaker at 35 °C and 120 rpm, following the procedure reported by Fang et al. (1995). The SMA analyses were conducted in triplicate for each calcium concentration. Methane production was measured every certain hour using a glass gas displacement device filled with 3 mol/L of NaOH solution. SMA was calculated from the linear range of the specific methane production rate curve using linear regression. The degrees of inhibition of SMAs under different calcium concentration are using specific methanogenic activity ratio (SMA_r) to determine, as shown in equation (1).

$$SMA_r = SMA_s/SMA_k \times 100\% \quad (1)$$

where SMAs stands for the SMA of granular sludge under different calcium concentrations, SMA_k stands for the SMA of granular sludge under no calcium addition media, which is called blank.

2.4. Analytical methods

COD, BOD_5, TSS, VSS, total N (TN), total P (TP), and NH_4^+-N were determined using standard methods (APHA et al., 1998). Volatile fatty acids (VFAs) were measured by titration (Anderson and Yang, 1992). pH was measured with a Thermo Orion 3-Star pH meter. Calcium concentrations were analyzed using a Dionex-4500i Ion Chromatogram with an IonPac AS14 column.

2.5. SEM and EDS analysis

For SEM and EDS analysis, granules were fixed for 2 h in 2.5% glutaraldehyde. After rinsing twice with sodium cacodylate buffer, the granules were fixed for 1.5 h in 1% osmium tetroxide. After rinsing with demineralized water, the aggregates were dehydrated in an ethanol series (10, 30, 50, 70, 90 and 100%, 20 min per step) and subsequently critical-point dried with carbon dioxide. At last, the aggregates were coated gold/palladium sputter, before examining on a SEM (JSM6300F, Jeol).

2.6. XRD analysis

XRD patterns were recorded over a 2 h from 10° to 90° in a scan rate of 3°/min using nickel-filter Cu Kα radiation ($\lambda = 0.15418$ nm)