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Changes of heavy metal speciation during high-solid anaerobic digestion of sewage sludge

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HIGHLIGHTS

- ▶ High-solid anaerobic digestion of sewage sludge was conducted in batch mode.
- ▶ Changes of heavy metal fractions and major parameters were investigated.
- ▶ The relationship between heavy metal fractions and these parameters were discussed.

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ABSTRACT

The sequential extraction procedure developed by Tessier et al. was used in sludge anaerobic digestion to determine the heavy metal speciation. Sludge samples were taken every three days to investigate humic substances, VS/TS, pH, VFA, alkalinity, ammonia, the total content of Zn, Pb, Cu, Ni, and Cr, and also their distribution into EXCH, CARB, FeMnOx, OMB and RESI fractions. Results showed that, (1) Heavy metals were concentrated during the anaerobic digestion process. The concentration of all five kinds of heavy metals increased by about 50%. (2) The distribution of these heavy metals differed. (3) High-solid anaerobic digestion much or less increased the bioavailability of Cu, Zn, Ni and Cr while decreased the bioavailability of Pb. (4) There were significant degrees of correlation between heavy metal fractions and changes of some selected parameters (for example, pH, VS/TS, and VFA content). Except for Pb, the contents of total mobile fractions for Cu, Zn, Ni, Cr could be predictable from its total content.

1. Introduction

With the rapid development of population and urbanization, a large amount of sludge, one major byproduct of biological wastewater treatment process, is produced in China. It seems to be a good idea to use such sludges as fertilisers or as organic soil regenerators because it could enable valuable components (organic matter, N, P, K and other nutrients necessary for plant growth) to be recycled (Gao et al., 2008; Roca-Pérez et al., 2009). However, there is a concern that high heavy metal content in sludge may threaten the environment as these elements are non-degradable and toxic (Karvelas et al., 2003; Wei and Liu, 2005). It has been pointed out that the determination of total heavy metal content is not enough to indicate its bioavailability, mobility and toxicity (Hsu and Lo, 2001; Amir et al., 2005). Actually, bioavailability and toxicity of heavy metals are more often dependent on their chemical forms (Nomeda et al., 2008; He et al., 2009a,b). Thus, it is necessary to reduce the bioavailability of heavy metals in sludge for safe land application.

High-solid anaerobic digestion is commonly characterized by a low moisture content of the feedstocks, typically less than 85% (w/w) (Rapport et al., 2008) and has been claimed to have more advantage over traditional low-solid anaerobic digestion for several reasons, such as smaller reactor volume, lower energy requirements for heating, less material handling, and so on (Guendouz et al., 2008). As more than 80% of the sewage sludge in China has already been dewatered before further disposal or treatment, low-solid anaerobic digestion was not well applied in China and high-solid anaerobic digestion could be one viable option to solve the sludge disposal problems (Duan et al., 2012).

Various methods for removal and dissolution of heavy metals have been used prior to land application of sewage sludge, including chemical extraction, bioleaching process, electrokinetic process, supercritical extraction and so on (Solisio et al., 2002; Chen et al., 2005).However, all these methods are expensive and generates toxic by-product. On the contrary, anaerobic digestion, as a major stabilization process, has been widely used for the treatment of different types of biosolids. Reduced bioavailability and crop uptake of heavy metals from digested sludge compared with raw

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sewage sludge were observed. It has been reported that decrease of bioavailability during composting is attributed to the formation of stable metal–humus complexes (Zheng et al., 2007; Tandy et al., 2009; Kang et al., 2011), which may also be applied to anaerobic digestion. Besides, some other factors may be related to the decrease of heavy metal bioavailability, including pH, VS, TS, VFA and so on (Amlinger et al., 2003; Soumare et al., 2003; Grigatti et al., 2004; Amir et al., 2005).

Most of the studies on the chemical speciation of heavy metals have been carried out just in raw, composted or digested sludge (Kunito et al., 2001; Maboeta and van Rensburg, 2003; Hanc et al., 2009). Only a few were dedicated specifically to study the bioavailability of the heavy metals during composting or anaerobic digestion of sewage sludges (Amir et al., 2005; Liu et al., 2007; Tandy et al., 2009). Studies relating changes in bioavailability of heavy metals with transformation in organic matter and humus fractions during composting or anaerobic digestion are scarce (Amir et al., 2005; Liu et al., 2007; Mahdi et al., 2009; Florencio et al., 2012).

In this study, high-solid anaerobic digestion of sewage sludge was conducted to determine the changes of heavy metal fractions and major parameters such as pH, VS/TS, VFA, ammonia, alkalinity and humic substances after which to discuss the relationship between the conversion of heavy metal fractions and these parameters.

2. Methods

2.1. Substrates and inoculums

Dewatered sewage sludge collected at the dehydration machine room of Anting wastewater treatment plant in Shanghai was used as substrate for this study. The sludge was obtained by collecting primary and excess sludge and dewatered with the aid of a high-molecular flocculant based on polyacrylamide. The total solids (TS) of the dewatered sludge was 22.3% (w/w) and volatile solids (VS) accounted for 56% of TS. The mesophilic seed sludge was samples from anaerobic digester with a volume of 6.5 L that has been operated for 4 months and it was used as an inoculum for digestion process. It had TS of 17% (w/w) and VS was 47% of TS.

2.2. Reactors and operation

Three identical reactors (numbered R1, R2 and R3) of 6.5 L total volume each of 6.0 L working volume were equipped with helix-type stirrers, which were set at a rate of 60 rpm (rotations per minute) with 10 min stirring and 10 min break continuously. Volumes of produced biogas were measured by wet gas meters every day.

On the first day of the experiments, 3 kg dewatered sludge and 2.8 kg seed sludge was added to each reactor, which was operated in batch mode at 35 ± 1 °C. The experiments continued until the biogas production stopped.

2.3. Chemical analysis

Sludge samples was taken out to determine chemical and physical properties such as pH, TS, VS, volatile fatty acid (VFA), total alkalinity (TA), ammonia, humic substances and heavy metal content every three days. Methane content of the biogas was measured by a gas chromatograph (GC) (Agilent Technologies 6890N, CA, USA) with a thermal conductivity detector equipped with Hayseq Q mesh and Molsieve 5A columns once a week. To analyze VFAs, the sludge samples from the reactors were centrifuged at 10,000 rpm for 10 min. Then the supernatant was passed through a microfiber filter (0.45 μm) and the filtrate was acidified by formic acid to adjust the pH to approximately 2.0 before VFA was analyzed by a GC (Agilent Technologies 6890N, CA, USA) with flame ionization detector. TS, VS, TA and ammonia were determined according to standard methods (APHA, 1995). The humic carbon extracted by 0.1 M NaOH solution was measured after oxidation by $KMnO_4$ (Bernal et al., 1996).

For determining the total heavy metal concentration in sludge before and after anaerobic digestion, a known quantity (1 g) of sample was digested with 14 ml of $HCl + HNO_3 + HF + HClO_4$ (1:4:1:1) at 180 °C. After the completion of the digestion, the samples were vacuum filtered and the filtrate was used for the determination of heavy metal concentration using Perkin Elmer Optima 2100 DV ICP-AES.

The chemical fractions of heavy metals were determined by the use of the sequential extraction procedure of Tessier et al., 1979, which is widely used in various studies of composting (Luo and Christie, 1998; Zheljazkov and Warman, 2003; Ciba et al., 2003; Amir et al., 2005). The steps are listed below.

(i) Exchangeable (EXCH). The sludge was extracted at room temperature for 1 h with 8 mL of magnesium chloride solution (1 M $MgCl_2$, pH 7.0) with continuous agitation.
(ii) Bound to Carbonates (CAR). The residue from (i) was leached at room temperature with 8 mL of 1 M NaOAc adjusted to pH 5.0 with acetic acid. Continuous agitation was maintained and the time necessary for complete extraction was evaluated.
(iii) Bound to Fe–Mn Oxides (FeMnOx). The residue from (ii) was extracted with 20 mL of 0.04 M $NH_2OH–HCl$ in 25% (v/v) HAc. The experiments were performed at 96 °C with occasional agitation and the time needed for complete dissolution of the free iron oxides was evaluated.
(iv) Bound to Organic Matter (OMB). To the residue from (iii) were added 3 mL of 0.02 M HNO_3 and 5 mL of 30% H_2O_2 adjusted to pH 2 with HNO_3, and the mixture was heated to 85 ± 2 °C for 2 h with occasional agitation. A second 3 mL aliquot of 30% H_2O_2 (pH 2 with HNO_3) was then added and the sample was heated again to 85 ± 2 °C for 3 h with intermittent agitation. After cooling, 5 mL of 3.2 M NH_4OAc in 20% (v/v) HNO_3 was added and the sample was diluted to 20 mL and agitated continuously for 30 min.
(v) Residual (RES). The residue from (iv) was digested with $HCl + HNO_3 + HF + HClO_4$ (1:4:1:1) at 180 °C and then determined using Perkin Elmer Optima 2100 DV ICP-AES.

Between each extraction, the samples were centrifuged (5000 rpm for 30 min) and filtered. The filtrate was digested with $HCl + HNO_3 + HF + HClO_4$ (1:4:1:1) at 180 °C before being used for the determination of heavy metal concentration using Perkin Elmer Optima 2100 DV ICP-AES.

As Tessier et al. (1979) described, there are four mobile fractions of heavy metals: exchangeable, susceptible to changes in ionic composition of water; Bound to Carbonates, susceptible to pH changes; Bound to Fe–Mn Oxides, unstable in reducing conditions; Bound to Organic Matter, which may be decomposed under oxidizing conditions and results in a release of the metals into the soil solution (Ciba et al., 2003). The fifth one is Residual in which metals are stably bound in the crystal lattice of the mineral components of the compost. Under normal conditions, the metals from residual cannot enter the food chain; therefore, residual fraction makes little contribution to the heavy metal bioavailability.

According to Liu et al. (2007), $C(a)$ and $C(T)$ are defined as the total concentration of mobile fractions and the total concentration of the heavy metal, in mg kg^{-1}(dry matter) φ as the ratio of $C(a)$ to $C(T)$, which can reflect the bioavailability of one heavy metal:

$$C(a) = C(1) + C(2) + C(3) + C(4) \tag{1}$$