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Effect of energy grass on methane production and heavy metal fractionation during anaerobic digestion of sewage sludge

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ABSTRACT

Anaerobic digestion (AD) is one of the most widely used processes to stabilize waste sewage sludge and produce biogas as renewable energy. The relatively low organic matter content and high heavy metal concentrations in sewage sludge have severely restricted the application and development of AD technology in China. In this study, the effect of energy grass (*Pennisetum alopecuroides*) addition on methane production and heavy metal fractionation during the AD of sewage sludge was evaluated. Methane production was enhanced by 11.2% by the addition of *P. alopecuroides*. The addition of *P. alopecuroides* significantly reduced the percentages of the water-soluble and exchangeable fractions of the target heavy metals in the sewage sludge after AD, and the dominant species were concentrated in Fe-Mn oxide-bound and organic- and sulfide-bound fractions of the digested sludge. The addition of *P. alopecuroides* at a dosage of 0.3 kg significantly ($P < 0.05$) decreased the mobility factors (MFs) of the target heavy metals after AD. In particular, the MFs of Cr and Ni were 61% and 32% lower, respectively, relative to the control. The increase in the added dose did not necessarily lead to further decreases in the MFs of the heavy metals. These results demonstrate that an appropriate addition of energy grass could enhance AD, decrease the mobility of heavy metals and promote heavy metal stabilization in sewage sludge during AD, which is beneficial for the subsequent land application of sewage sludge.

1. Introduction

Due to the increasing production and treatment of domestic and industrial wastewater, a massive amount of sewage sludge has been generated and discharged to the environment. Statistics indicate that more than 11.2 M t of dry municipal sludge is produced annually in China, and that amount is expected to increase at a rate of 10% per year (Fang and Cen, 2010). The treatment and disposal of sewage sludge have become great challenges in environmental management across the globe, which is especially true for developing countries. Sewage sludge contains abundant nutrients and organic substances that are indispensable to plants. Land application of sewage sludge is becoming increasingly feasible because of its many benefits including increasing soil fertility and improving soil structure (Caicedo et al., 2015; Westerhoff et al., 2015). Due to certain hazardous substances such as heavy metals, organic pollutants, and pathogenic bacteria, its direct application of untreated sewage sludge to land has been prohibited in many countries (Dąbrowska and Rosińska, 2012). Heavy metals are the primary pollutants in sewage sludge and present a serious environmental problem (Demirbas et al., 2005; Tu et al., 2012). Compared with certain antibiotics and organic contaminants, heavy metals (such as cadmium (Cd), zinc (Zn), chromium (Cr) and other elements) are difficult to bio-degrade and easily accumulate along the food chain (Yuan et al., 2011; Zhao et al., 2014). Sludge should undergo chemical and hygienic stabilization before land application (Singh and Agrawal, 2009; Walter et al., 2006).

Anaerobic digestion (AD) is a widely used technology for the efficient treatment of sewage sludge, simultaneously generating renewable energy through the conversion of organic matter into methane (Choong et al., 2016; Liu et al., 2012). However, a poor organic matter content and low C/N ratio (carbon-to-nitrogen ratio) of sewage sludge often result in a low AD efficiency (Yu et al., 2016). The low C/N ratio in sludge could result in the accumulation volatile fatty acids (VFA) and total ammonia nitrogen (TN) in digesters, thereby decreasing the activity of methanogens (Mata-Alvarez et al., 2000). One method to overcome its

Abbreviations: AD, anaerobic digestion; TS, total solids; VS, volatile solids; VFA, volatile fatty acids; C/N, carbon-to-nitrogen ratio; MFs, mobility factors.

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recalcitrant properties is to adjust low sludge C/N ratio by adding high-carbon-content materials such as waste paper (Yen and Brune, 2007; Beltrán et al., 2016). Anaerobic co-digestion of sewage sludge with other organic waste appears to be especially attractive because of its multiple benefits such as improving the balance of nutrients, increasing the load of biodegradable organic matter and better biogas yields (Mata-Alvarez et al., 2014). Besides, AD increased the bioavailability of copper (Cu), Zn, nickel (Ni) and Cr in sewage sludge in a recent study (Dong et al., 2013), which may pose an ecological risk after land application.

Pennisetum alopecuroides is an inexpensive and green environmental material that has been widely used in the field of environmental remediation and biomass energy production in European and American countries (Kang et al., 2016). Because *P. alopecuroides* has high carbon content, adding it into an anaerobic environment may balance the C/N ratio of sewage sludge and consequently improve the AD efficiency of the sludge (Tandy et al., 2009). *P. alopecuroides* contains functional acidic groups, such as carboxyl groups, and its hydrolysis products may have significant influence on the adsorption of heavy metals through the formation of stable chelates, thereby contributing to the immobilization of heavy metals in sewage sludge (Kang et al., 2016). Therefore, it can be hypothesized that *P. alopecuroides* addition may also improve the stabilization of heavy metals in sewage sludge during anaerobic co-digestion.

To the best of our knowledge, studies to determine the effects of energy grass on the AD process and stabilization of heavy metals are limited (Tandy et al., 2009). Few studies have focused on the effects of *P. alopecuroides* addition on biogas yields and dynamic changes in the chemical species distribution of heavy metals during AD. The objectives of the present study were as follows: (1) to investigate the effects of the anaerobic co-digestion of sewage sludge with *P. alopecuroides* on biogas (methane) production; (2) to study the dynamic changes in heavy metals species during anaerobic co-digestion using a sequential extraction procedure; and (3) to evaluate the effectiveness of energy grass addition on the mobility and bioavailability of heavy metals in the end products of AD.

2. Materials and methods

2.1. Sewage sludge and energy grass

Dewatered sewage sludge collected from a local municipal wastewater treatment plant in Hefei, Anhui Province, China, was used as the feeding substrate in the present study. The total solids (TS) were 10.3 ± 0.32% (w/w), and the volatile solids (VS) in the sludge were 55.6 ± 0.68% of the TS. The C/N ratio of the investigated sludge was 4.8 ± 0.2. The total contents of the heavy metals in the sludge were 132.5 ± 11.3 mg kg^{-1} Cr, 157.1 ± 12.9 mg kg^{-1} Cu, 81.9 ± 7.12 mg kg^{-1} Mn, 62.8 ± 9.11 mg kg^{-1} Ni and 1962.8 ± 78.5 mg kg^{-1} Zn. Anaerobic sludge was collected for use as the seed solution from the anaerobic digester that has been operated with mesophilic (35 °C) conditions for 3 months in the National Engineering Research Center for Urban Pollution Control (NERCUPC) at Tongji University. The main characteristics of the anaerobic biomass used as inoculums were: pH, 7.3 ± 0.2; total solids (TS), 9.2 ± 0.3% (w/w) and VS were 47.6 ± 1.2% of TS. The energy grass (*P. alopecuroides*) used in the study was obtained from the Laboratory for Energy Grass Research at Fujian Agricultural and Forestry University. The plants were air-dried, ground and sieved to 20-mm mesh. Plant carbon, hydrogen and nitrogen contents of 41.9% ± 6.52%, 5.8% ± 0.78% and 1.6% ± 0.25%, respectively, were determined using a Leco CHNS-932 elemental analyzer (Leco Corporation, St. Joseph, MI, USA). The C/N ratio of the energy grass was 25.9 ± 4.23, and the ash content was 9.3% ± 0.78%.

2.2. Design and operation of the anaerobic reactors

The batch experiments were performed in double-walled cylindrical vessels with a working volume of 6.5 L. Helix-type stirrers were installed and operated at a rate of 60 rpm (rotations per minute), with 10 min of stirring and 5 min of continuous breaking intervals. Initially, each reactor was sparged with nitrogen gas for approximately 6 min after loading the mixture of inoculum and raw sludge with a ratio of 1:3 (based on the VS). Three sets of batch experiments were designed as follows: 5.8 kg of sludge without energy grass addition (R1), 5.8 kg of sludge and 0.3 kg of *P. alopecuroides* (R2), and 5.8 kg of sludge and 0.5 kg of *P. alopecuroides* (R3). Each treatment had three parallel reactors. The three sets of identical reactors were all operated under mesophilic temperature conditions (35 ± 1) °C.

The whole cycle of the digestion progress lasted 30 days. The biogas volume produced from each reactor was recorded daily, and the methane content was analyzed every three days using a gas chromatograph (GC) (Agilent 6890N, Agilent Technologies, CA, USA) with a thermal conductivity detector. Approximately 30 g of the sludge samples were removed from each reactor every three days and stored at 4 °C prior to chemical analysis. Part of each collected sludge sample was centrifuged and passed through a microfiber filter (0.22 μm), and the filtrate was acidified with formic acid for physiochemical analysis. The TS, VS, pH, VFA, alkalinity, and ammonia content were determined following standard methods (APHA, 1995). The remaining sludge was freeze-dried, ground and sieved through a 2-mm mesh for analysis of the chemical speciation and contents of heavy metals. All of the chemical reagents used in this work were analytical grade.

2.3. Metal extraction and chemical speciation

To determine the total concentration of heavy metals, including Zn, Ni, Cr, Mn and Cu, 0.5 g of the dry sludge samples were digested with aqua regia in a Teflon tube at 180 °C for 3 h. After digestion, the samples were filtered through 0.22-μm filter membranes, and the filtrate was used to determine the total metals content by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Perkin Elmer Optima 2100 DV ICP-AES). Sequential extraction of the heavy metals in the sludge was performed based on the method by Tessier et al. (1979) with some modifications. A 1.0-g sludge sample was first dissolved in deionized water and then shaken for 16 h. The mixture was centrifuged at 3000 rpm for 30 min and then filtered through a 0.22-μm membrane filter. The heavy metals in the supernatant were defined as the water-soluble fraction. The residue was subjected to Tessier's four-step extraction procedure to fractionate the exchangeable, carbonate-bound, iron-manganese (Fe-Mn) oxide-bound, organic- and sulfide-bound, and residual fractions. The speciation method to determine the six chemical fractions is outlined in Table 1. The

Table 1
Tessier's four-step extraction procedure with modification for heavy metal speciation analysis in the sewage sludge.

Principal extracted component	Reagent and its concentration	Extraction conditions		
		pH	T (°C)	Time (h)
Water-soluble	Deionized water	7.0	25 ± 0.5	3
Exchangeable	1 M NH_4OAc	7.0	25 ± 0.5	8
Carbonate-bound	1 M NaOAc	5.0	25 ± 0.5	8
Fe-Mn oxide-bound	0.1 M $NH_2OH.HCl$	2.0	25 ± 0.5	16
Organic- and sulfide-bound	30% H_2O	2.0	85 ± 5	2
	1 M NH_4OAc	2.0	25 ± 0.5	

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