JOURNAL OF ENVIRONMENTAL SCIENCES 33 (2015) 29–38

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JOURNAL OF ENVIRONMENTAL SCIENCES

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Impact of ozone assisted ultrasonication pre-treatment on anaerobic digestibility of sewage sludge

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ARTICLE INFO

Article history:
Received 30 October 2014
Revised 13 January 2015
Accepted 14 January 2015
Available online 11 April 2015

Keywords:
Sewage sludge
Ultrasound
Ozone
Pre-treatment
Molecular weight
Anaerobic digestion

ABSTRACT

Impact of ultrasonication (ULS) and ultrasonication–ozonation (ULS-Ozone) pre-treatment on the anaerobic digestibility of sewage sludge was investigated with semi-continuous anaerobic reactors at solid retention time (SRT) of 10 and 20 days. The control, ULS and ULS-Ozone reactors produced 256, 309 and 348 mL biogas/g COD_{fed} and the volatile solid (VS) removals were 35.6%, 38.3% and 42.1%, respectively at SRT of 10 days. At SRT of 20 days, the biogas yields reached 313, 337 and 393 mL biogas/g COD_{fed} and the VS removal rates were 37.3%, 40.9% and 45.3% in the control, ULS and ULS-Ozone reactors, respectively. ULS-Ozone pre-treatment increased the residual organic amount in the digested sludge. These soluble residual organics were found to contain macromolecules with molecular weights (MW) larger than 500 kDa and smaller polymeric products with MW around 19.4 and 7.7 kDa. These compounds were further characterized to be humic acid-like substances with fluorescent spectroscopy analysis.

Introduction

Ultrasonication (ULS) has been reported to be an effective sludge pre-treatment (*i.e.* treatment of pre-digestion feed sludge) technology (Tiehm et al., 1997, 2001). Biological flocs in the sludge matrix are mechanically disrupted, resulting in particle size reduction and solubilization of extra/intra-cellular polymeric substances (Bougrier et al., 2005; Wang et al., 2006b). Consequently, methane production and solids removal efficiency during the subsequent sludge anaerobic digestion are improved (Tiehm et al., 1997, 2001). In spite of its advantages, ULS pre-treatment has limitation because it is essentially "single" effect — mechanical disintegration (Khanal et al., 2007; Lehne et al., 2001). Enhancement of the effectiveness of ULS pre-treatment had been attempted by combining ULS process with chemical pre-treatment methods. Combination of ULS pre-treatment with alkaline (Chiu et al., 1997; Jin et al., 2009; Kim et al., 2010) and acidic pre-treatments (Liu et al., 2008; Sahinkaya, 2014) has been demonstrated to increase sludge disintegration as well as the subsequent anaerobic digestion.

Apart from the aforementioned chemical methods, ozone has also been shown feasible to enhance the ultrasonic pre-treatment (Tian et al., in press; Xu et al., 2010; Yang et al., 2012, 2013). Xu et al. (2010) demonstrated the feasibility of combining ultrasound and ozone to disintegrate waste activated sludge (WAS) and to improve the methane recovery from the

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http://dx.doi.org/10.1016/j.jes.2015.01.003
1001-0742/

subsequent anaerobic digestion. Yang et al. (2013) observed the combined ultrasound and ozone pre-treatment enhanced the solubilization of amino acids and proteins in WAS. Tian et al. (in press) found that ozone was able to chemically degrade macromolecules solubilized by ultrasound and further increased the sludge anaerobic biodegradability.

These previous studies had focused on characteristics of the solubilized compounds and changes in sludge properties after pre-treatment. Xu et al. (2010) and Tian et al. (in press) did, however, investigate the influence of pre-treatment on sludge anaerobic biodegradability in batch serum bottle tests. Information on the influence of such combined pre-treatment on solid removal efficiency and digested sludge characteristics after anaerobic digestion is not available. Besides, influence of solid retention time (SRT), an important design parameter, on the anaerobic digestion of the combined pre-treated sludge has also not been reported. This work aims to investigate the impact of such pre-treatment on the subsequent anaerobic digestion process with semi-continuous reactors at SRT of 10 and 20 days. Biogas production and solid concentrations in the digested sludge were monitored to assess the possible enhancement with such pre-treatment. Molecular weight (MW) distribution and fluorescent spectroscopy analysis were conducted to provide more information on the soluble residual organics in the digested sludge.

1. Materials and methods

1.1. Sludge samples

Samples of a mixture of primary sludge and thickened WAS (ratio around 1:1 based on dry solids) were collected from a local municipal wastewater reclamation plant. The characteristics of the sewage sludge samples are as shown in Table 1.

1.2. Analytical methods

COD and solid concentrations were measured in accordance with Standard Methods (APHA, 1998). Sludge dewaterability was measured with capillary suction time (CST) as described in Standard Methods (APHA, 1998). Sludge pH was measured with a pH meter (model 3200P, Agilent, Santa Clara, CA, USA). A UV spectrophotometer (UV-1800, Shimadzu, Kyoto, Japan) was used in the determination of proteins, carbohydrates and ammonia-nitrogen concentrations. Proteins concentration was determined with the method of Lowry et al. (1951). Carbohydrates concentration was determined colorimetrically with the phenol-sulphuric acid method (DuBois et al., 1956). Ammonia-nitrogen was measured colorimetrically using Nessler's reagent. VFAs concentration was analyzed with a gas chromatograph (7890A GC system, Agilent, Santa Clara, CA, USA) fitted with a flame ionization detector. The composition of biogas was measured with a gas chromatograph (7890A GC system, Agilent, Santa Clara, CA, USA) with thermal conductivity detectors.

Table 1 – Main characteristics of the untreated sewage sludge.

Parameters	Value range
Total solids (g/L)	14.9–15.4
Total suspended solids (g/L)	13.7–14.1
Volatile solids (g/L)	12.7–13.2
Volatile suspended solids (g/L)	11.8–12.0
Total COD (g/L)	17.4–20.0
Soluble COD (g/L)	0.82–1.26
pH	5.9–6.2

1.3. Pre-treatment conditions

The pre-treatment conditions were selected following consideration of the results of a previous study (Tian et al., in press). ULS pre-treatment was performed with an ultrasonicator (Q700, Misonix, Newton, CT, USA) with a frequency of 20 kHz. The temperature was monitored and maintained at 30°C with an ice-water bath during ultrasonication. The specific energy input was 9 kJ/g total solids (TS). Ozonation pre-treatment was performed with an ozone generator (WEDECO GSO 30, Xylem, Herford, Germany). Pure oxygen was used as feed gas and converted to ozone with a high voltage converter. A stone diffuser was used to produce fine ozone bubbles and enhance ozone mass transfer. The applied ozone dosage was 0.012 g O_3/g TS. Ultrasonication–ozonation (ULS-Ozone) pre-treatment was performed by sequentially applying the ULS and the ozonation treatments at the aforementioned dosages.

1.4. Molecular weight distribution

MW distribution was measured in accordance with Tian et al. (in press). A high performance liquid chromatograph (1260 LC system, Agilent, Santa Clara, CA, USA) was used for MW distribution analysis using the PL aquagel-OH 8-μm MIXED-M column. Milli-Q water was used as mobile phase with a flow rate of 1 mL/min. A PL aquagel-OH 8-μm guard column was installed in front of the main column. The sample was first centrifuged at 10,000 r/min for 10 min and then filtered through a 0.2 μm membrane filter before injection. A UV (254 nm) detector was used for the detection of the eluted substances. Corresponding MW of a detected peak was calculated by converting its retention time to the corresponding MW as shown in Eq. (1) (Tian et al., in press):

$$\log(\mathrm{MW}) = 9.8223–0.6748(\mathrm{Rt}) \quad (1)$$

where, Rt (min) is the retention time of the detected peaks and MW (Da) is the molecular weights of the compounds detected in the corresponding peaks.

1.5. EEM fluorescence spectroscopy analysis

A fluorescence spectrometer (LS 55, Perkin Elmer, Waltham, MA, USA) was used to measure the fluorescence intensity (FI) of the soluble fluorescent products. The measurement procedure was previously described by Wu et al. (2011). Excitation wavelength (Ex) was from 230 to 520 nm with 5-nm intervals. Emission wavelength (Em) was collected from 230 to 550 nm with 5-nm increments. Samples were pre-diluted 10 times with DI water to avoid the measured FI exceeding the maximum level.