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Insights on the solubilization products after combined alkaline and ultrasonic pre-treatment of sewage sludge

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ABSTRACT

This work provides insights on the solubilization products after a simultaneous combination of alkaline and ultrasonic (ALK + ULS) pre-treatment of sewage sludge. Soluble chemical oxygen demand (SCOD) increased from 1200 to 11,000 mg/L after such treatment. Organics with molecular weight around 5.6 kDa were solubilized because of the synergistic effect of ultrasound and alkali. Organics with molecular weight larger than 300 kDa increased from 7.8% to 60%, 16% and 42.3% after ULS, ALK and ALK + ULS treatment, respectively. Excitation emission matrix fluorescence spectroscopy analysis identified soluble microbial product-like and humic acid-like matters as the main solubilization products. Sludge anaerobic biodegradability was significantly enhanced with the simultaneous application of ALK + ULS pre-treatment. ALK + ULS pre-treatment resulted in 37.8% biodegradability increase compared to the untreated sludge. This value was higher compared to the biodegradability increase induced by individual ALK pre-treatment (5.7%) or individual ULS pre-treatment (20.7%) under the same conditions applied.

Introduction

Sludge is a by-product of wastewater treatment which requires further treatment and disposal. Anaerobic digestion is often used given its advantages of high degree of organic stabilization and methane production (Gronroos et al., 2005). Anaerobic digestion is, however, a relatively slow process. Much of the sludge organics are particulate macromolecules and can only pass through cell membranes and be utilized by microorganisms when hydrolyzed into soluble simple organics (Pavlostathis and Giraldo-Gomez, 1991). Hydrolysis of particulate macromolecules is the rate-limiting step in sludge anaerobic digestion (Eastman and Ferguson, 1981; Pavlostathis and Giraldo-Gomez, 1991). The hydrolysis of waste activated sludge (WAS) is especially slow because of its composition. WAS comprises intact microbial cells which are enclosed by extracellular polymeric substances (EPS) and other organic fibers. This complex structure protects microorganisms from being lyzed and thus slows hydrolysis. In order to overcome this rate-limiting step, pre-treatment processes are often applied to solubilize the sludge for anaerobic digestion.

Ultrasonic (ULS) pre-treatment, a mechanical process, has been reported to be an effective sludge pre-treatment method (Tiehm et al., 1997). The collapse of cavitation bubbles during

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ultrasonication imposes substantial hydro-mechanical shear force on the particulate matters in sludge. This mechanical force breaks up biological flocs and ruptures microbial cells, resulting in solubilization of intracellular and extracellular polymers.

Chemical oxygen demand (COD) solubilization during ultrasonication process could be significantly enhanced with the aid of NaOH addition (Chiu et al., 1997). Wang et al. (2005) confirmed that higher ultrasonic sludge disintegration was obtained at a higher pH with the multi-variable linear regression method. Synergistic increase in sludge disintegration degree (DD) was observed when alkaline (ALK) and ULS pre-treatments were applied simultaneously (Kim et al., 2010). Notwithstanding these reports, there is a relative lack of fundamental knowledge on the characteristics of the solubilized compounds following such combined pre-treatment process. This work aims to shed more light on the solubilization products in terms of molecular weights (MWs) and fluorescence intensities.

MWs of the solubilized organics are important as these may impact on the downstream biological process (Eskicioglu et al., 2006). Size exclusion chromatography (SEC) has been used to measure MW of organic substances in water samples (Aquino et al., 2006; Her et al., 2003; Trzcinski et al., 2011). However, such approach has not yet been reported for the assessment of the change in soluble organics due to a pre-treatment step. Therefore, SEC measurement was conducted in this work to characterize the MW of solubilized substances after pre-treatment. Afterwards, the soluble organics were fractionated into different MW ranges with ultrafiltration (UF) membranes. COD of each MW fraction was determined to complement the SEC results. Excitation emission matrix (EEM) was an emerging technique used to characterize the solubilization products after the sludge pre-treatment process (Luo et al., 2013; Yang et al., 2013). However, relevant research on its application to characterize the solubilization products following ALK + ULS pre-treatment has not been reported. Therefore, EEM fluorescence spectroscopy analysis was conducted in this study to fill the information gap. Fluorescence intensities of soluble microbial product (SMP) and humic acid (HA) substances were measured to provide novel insights on the solubilization products after ALK + ULS pre-treatment. Anaerobic digestion tests were also conducted to investigate the influence of the solubilized substances on subsequent anaerobic digestion.

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, total solids (TS): 15–17 g/L) were collected from a local municipal used water treatment plant. Sludge pH was relatively constant, varying from 6.3 to 6.5.

1.2. Analytical methods

COD was measured in accordance with Standard Methods (APHA, 1998). Protein concentration was determined with Lowry et al. (1951) using a UV spectrophotometer (UV-1800, Shimadzu, Kyoto, Japan) against a blank at wavelength 750 nm. Bovine serum albumin was used as the standard. Carbohydrate concentration was determined with the sulfuric-phenol method (DuBois et al., 1956) against a blank at wavelength 495 nm. D-Glucose was used as the standard. Protein and carbohydrate concentrations were converted to equivalent COD concentration with factors of 1.5 and 1.07, respectively as described previously (Rittman and McCarty, 2001). TOC was analyzed with a Multi N/C 2100S TOC analyzer (Analytik-Jena, Jena, Germany). Sludge pH was measured with a pH meter (3200P, Agilent, Santa Clara, CA, USA). Sludge DD was expressed as the extent of sludge solubilization. It was calculated as follows (Muller et al., 1998):

$$DD = (SCOD_T - SCOD_0)/(SCOD_{NaOH} - SCOD_0) \times 100\% \quad (1)$$

where $SCOD_T$ is the soluble chemical oxygen demand (SCOD) of treated sample, $SCOD_{NaOH}$ is the SCOD of sample immersed in 1 mol/L NaOH (1:1, *V/V*) at 90°C for 10 min and $SCOD_0$ is the SCOD of the untreated sample.

1.3. Sludge pre-treatments

NaOH was selected for ALK pre-treatment due to its reported higher impact on sludge (Kim et al., 2003). Sodium hydroxide pellets were dissolved to make a 3 mol/L stock solution. Various NaOH concentrations were achieved by adding different volumes of stock solution to the sludge sample. Applied NaOH concentrations were 0.01, 0.02, 0.05 and 0.1 mol/L which corresponded with NaOH dosages of 0.025, 0.05, 0.125 and 0.25 g NaOH/g TS, respectively. The sludge samples were then mixed at 200 r/min for 10 min at room temperature (25°C).

ULS pre-treatment was performed with an ultrasonicator (Q700, Misonix Qsonica, Newton, CT, USA). The ultrasound frequency was 20 kHz with a maximum power input at 700 W. The power input was around 130 W when applied to a treated sludge volume of 200 mL. Ultrasonication energy was quantified in terms of specific energy input and the calculation is as follows (Lehne et al., 2001):

$$\text{Specific energy input} = (P \times t)/(V_{sludge} \times \text{TS}) \quad (2)$$

where, P (W) is the power input of the ultrasonicator, t (sec) is the time of ultrasonication, and V_{sludge} (L) is the volume of treated sludge. During ultrasonication, the temperature of the sample was monitored and maintained at about 30°C with an ice-water bath. The maximum specific energy input was 21 kJ/g TS.

ALK and ULS pre-treatments were conducted simultaneously (ALK + ULS), as ALK + ULS treatment had been reported to have higher impact on sludge compared to sequential combinations (Chiu et al., 1997; Jin et al., 2009). ALK + ULS pre-treatment was performed by sonicating the sludge while it was being mixed at a designated NaOH concentration.

1.4. Size exclusion chromatography

A high performance liquid chromatography (HPLC) (1260 LC system, Agilent, Santa Clara, CA, USA) was used for the SEC 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. The supernatant was then filtered through a 0.2 μm membrane filter before injection. UV (254 nm) detector was used for the detection of the eluted substances. Calibration was done using polyethylene glycol and polyethylene oxide standards with MW of 500 kDa, 70 kDa, 4 kDa, 600 Da and 106 Da. A linear