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Pretreatment of pulp mill secondary sludge for high-rate anaerobic conversion to biogas

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ABSTRACT

Three pretreatment methods were compared based on their ability to increase the extent and rate of anaerobic bioconversion of pulp mill secondary sludge to biogas. The pretreatment technologies used in these experiments were: (i) thermal pretreatment performed at 170 °C; (ii) thermochemical (caustic) pretreatment performed at pH 12 and 140 °C; and (iii) sonication performed at 20 kHz and 1 W mL^{-1}. Sludge samples were obtained from a sulfite and a kraft pulp mill, and biochemical methane potential (BMP) assays were performed using microbial granules obtained from a high-rate anaerobic digester operating at a pulp mill. Biogas production from untreated sludge was 0.05 mL mg^{-1} of measured chemical oxygen demand (COD) and 0.20 mL mg^{-1} COD for kraft and sulfite sludge, respectively. Thermal pretreatment had the highest impact on sludge biodegradability. In this case, biogas yield and production rate from sulfite sludge increased by 50% and 10 times, respectively, while biogas yield and production rate from kraft sludge increased by 280% and 300 times, respectively. Biogas yield correlated to soluble carbohydrate content better than soluble COD.

1. Introduction

Aerobic microorganisms catalyze the conversion of organic substances in wastewater to carbon dioxide, water, and microbial biomass, or secondary sludge. Roughly four million dry tonnes of secondary sludge are produced each year in the United States by pulp and paper mills that employ aerobic wastewater treatment systems (Scott and Smith, 1995). This sludge is typically dewatered and then disposed by land filling or incineration. Due to the high water content in the sludge even after dewatering, incineration often requires supplemental fuel. As a result, secondary sludge disposal can account for as much as 60% of total wastewater treatment costs (Kyllönen et al., 1988).

The cost of secondary sludge disposal is expected to increase particularly in North America and Europe, in response to higher wastewater treatment standards, reduced landfill capacities, increased fuel costs, and eminent emissions penalties. Mahmood and Elliott (2006) recently reviewed options to alleviate these costs by adopting processes that would reduce the production of secondary sludge, and technologies to convert sludge to useful products. For instance, the anaerobic bioconversion of pulp mill sludge to biogas was reviewed as a means to reduce sludge volume while generating renewable energy that can displace natural gas in industrial processes (Mahmood and Elliott, 2006; Deublein and Steinhauser, 2008).

Anaerobic bioconversion of organic compounds to biogas results from the concerted activity of fermentative bacteria and methanogenic Archaea (Hobson and Wheatley, 1993). The biogas that is generated typically contains 60–70% methane by volume (Deublein and Steinhauser, 2008). While anaerobic bioconversion has been employed for many years to treat municipal sewage sludge, the adoption of this technology by pulp and paper industries has been limited, mainly due to the 30–60 day residence times required to process the sludge in conventional bioreactors (Elliott and Mahmood, 2007). The upflow anaerobic sludge blanket (UASB) reactor is a high-rate anaerobic reactor that was developed in the early 1980s (Hobson and Wheatley, 1993). UASB reactors, and other high-rate anaerobic reactors, have hydraulic retention times (HRT) of hours rather than days. Microbial catalysts in these reactors form granules that remain suspended by the upward flow of incoming wastewater. Three-phase separators positioned near the top of the reactor remove the biogas, and promote the circulation of microbial granules and recycled wastewater. Given the low HRT, high-rate anaerobic reactors are smaller than conventional anaerobic bioreactors, and can be integrated with existing industrial processes with comparatively low capital expenditures (Hobson and Wheatley, 1993; Kleerebezem and Macarie, 2003).

Currently, high-rate anaerobic reactors account for approximately 50% of all industrial anaerobic reactors (Kleerebezem and Macarie, 2003). Of the more than 800 installations worldwide, approximately 75 high-rate reactors are located at pulp mills (Kleerebezem and Macarie, 2003). To date, anaerobic reactors at pulp mills are used to transform effluent that is rich in soluble

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organic substances, and not solid wastes such as secondary sludge. Pretreatment technologies, including high temperature, sonication, high-pressure homogenization, addition of acids and bases, or addition of enzymes, have been developed to solubilize the organic fraction of secondary sludge (Elliott and Mahmood, 2007; Barjenbruch and Kopplow, 2003; Bougrier et al., 2006; Chen et al., 2007; Khanal et al., 2007; Penaud et al., 1999; Tanaka et al., 1997; Valo et al., 2004). However, most reports that evaluate the potential of pretreatments to increase the anaerobic bioconversion of secondary sludge to biogas have used municipal sludge, and relatively few studies have compared different pretreatments using the same sludge samples (Elliott and Mahmood, 2007).

In addition to microbial biomass, pulp mill secondary sludge can contain residual cellulose, lignin and chemical components from the pulping process (Kyllönen et al., 1988). Given the compositional differences between municipal and pulp mill sludge, a systematic comparison of pretreatment technologies using pulp mill secondary sludge is required to assess the option of using high-rate anaerobic bioreactors to reduce sludge volume while producing biogas (Elliott and Mahmood, 2007). Accordingly, the objective of this study is to compare the impact of three pretreatment technologies on the rate and extent of anaerobic digestion of pulp mill secondary sludge, namely: (i) thermal treatment for 1 h at 170 °C, (ii) caustic treatment at pH 12 and 140 °C for 1 h, and (iii) sonication treatment at 20 kHz and an intensity of 1 W mL^{-1}. These pretreatment options are commercially available, and are known to significantly enhance the anaerobic digestion of municipal sludges. To our knowledge, this report represents the first systematic comparison of readily available pretreatment technologies for high-rate anaerobic bioconversion of pulp mill secondary sludge. We demonstrate that thermal and caustic pretreatment can increase the solubility and bioconversion potential of pulp mill secondary sludge. The impact of sludge quality on biogas production is also discussed.

2. Experimental section

2.1. Sludge samples

Secondary sludge samples were obtained from two Canadian pulp mills: one is an ammonium sulfite mill that applies a plug flow activated sludge wastewater treatment system and the other is a kraft mill that uses an aerated stabilization basin for its wastewater treatment system. The samples were stored in a refrigerator controlled at 4 °C.

2.2. Methanogenic culture

Anaerobic granules are microbial aggregates that form in upflow anaerobic sludge blanket reactors. In the current study, anaerobic granules were collected from a high-rate anaerobic bioreactor (Paques™ internal circulation (IC) reactors) installed at the sulfite mill, and were stored at 4 °C in 160 mL glass serum bottles sealed with butyl rubber stoppers and sparged with 80:20 nitrogen and carbon dioxide gas.

2.3. Pretreatment of sludge samples

2.3.1. Thermal pretreatment

Sludge samples (400 mL) were hydrothermally heated at 170 °C for 1 h. The headspace of the reactor was flushed with nitrogen gas to remove oxygen and prevent oxidation. After the thermal pretreatment, sludge samples were cooled to room temperature and the pH of the suspension was adjusted to pH 7 with HCl.

2.3.2. Caustic pretreatment

NaOH pellets were dissolved in 400 mL of each sludge sample to reach pH 12. The samples were heated to 140 °C for 1 h, and then cooled to room temperature and adjusted to pH 7.

2.3.3. Sonication pretreatment

A custom-manufactured tubular sonication unit from Advanced Sonics Processing Systems was used to pretreat 400 mL of each sludge sample at 20 kHz and power density of 1 W mL^{-1}. Ultrasonic vibration was delivered through a plate transducer; the effective power delivered to the samples was 0.60 W $(cm^2)^{-1}$ or 54.5 W, and the effective power density was 0.14 W mL^{-1} (Yong et al., 2008). The pretreatment progressed for 30 min, and the temperature of the treated samples did not exceed 55 °C. These conditions are consistent with applications used to pretreat municipal samples (Chu et al., 2001).

2.4. Characterization of sludge samples

The samples were analyzed for solids content, inorganic and organic nitrogen content, carbon, hydrogen, sulfate, sulfide, reactive phosphorus, and metal contents. Sludge samples were centrifuged at 8000 rpm using a Beckman Coulter Allegra 25R and TA 10-250 rotor, and filtered through a 0.45 μm pore Supor membrane. The filtrate and retentate were characterized as described below.

2.4.1. Suspended solids

Total suspended solids (TSS) and volatile suspended solids (VSS) were measured following Standard Methods for the Examination of Water and Wastewater (APHA, 1998). Briefly, Whatman 934-AH filters (pore size: 1.5 μm) were dried at 550 °C for 30 min. Once cooled, the filters were weighed and then used to filter a specified volume of sludge sample. The filter and retentate were dried at 103 °C for 2 h, weighed, transferred to 550 °C for 30 min, and then weighed again. TSS and VSS are calculated using the following equations:

$$\mathrm{TSS} = (m_{\text{After 103 °C}} - m_{\text{filter}})V^{-1}$$

$$\mathrm{VSS} = (m_{\text{After 103 °C}} - m_{\text{After 550 °C}})V^{-1}$$

where $m_{\text{After 103 °C}}$ is the mass of the filter and retentate after drying at 103 °C, m_{filter} is the mass of the filter, $m_{\text{After 550 °C}}$ was the mass of the filter and retentate after ignition at 550 °C, and V is the volume of sample filtered.

2.4.2. Chemical oxygen demand (COD)

COD was measured by following the Standard Method 5220D described in (APHA, 1998). Briefly, the digestion solution was prepared by adding 10.216 g K_2CrO_7, previously dried at 150 °C for 2 h, to 500 mL of water purified on a Milli-Q® system (Millipore®). A 167 mL aliquot of H_2SO_4 (98% A.C.S. reagent) and 33.3 g $HgSO_4$ were then added, and the mixture was allowed to dissolve and cool to room temperature. The solution was adjusted to 1 L with Milli-Q water. The sulfuric acid solution was prepared by mixing 5.5 g Ag_2SO_4 per kg concentrated (98%) H_2SO_4. Replicate 2.5 mL aliquots of a standard or test sample were transferred to HACH COD 16 mm test tubes with Teflon-lined screw-caps, and 1.5 mL of digestion solution and 3.5 mL of sulfuric acid solution were added to each tube. The tubes were over turned several times and then heated at 150 °C for 2 h. Once cooled to room temperature, absorbencies of resulting solutions were measured at 600 nm. A standard curve corresponding to 0.1–1.0 mg COD mL^{-1} was prepared using potassium hydrogen phthalate (KHP) that had been dried for 2 h at 110 °C. KHP has a theoretical COD of 1.176 mg COD mg^{-1}. When COD concentrations were below 0.1 mg mL^{-1}, the digestion solu-