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Pretreatment of municipal waste activated sludge for volatile sulfur compounds control in anaerobic digestion

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ABSTRACT

The effect of combination of mechanical and chemical pretreatment of municipal waste activated sludge (WAS) prior to anaerobic digestion was studied using a laboratory scale system with an objective to decrease volatile sulfur compounds in biogas and digested sludge. Mechanical pretreatment was conducted using depressurization of WAS through a valve from a batch pretreatment reactor pressurized at 75 ± 1 psi, while combined pretreatments were conducted using six different dosages of hydrogen peroxide (H_2O_2) and ferrous chloride ($FeCl_2$) along with mechanical pretreatment. About 37–46% removal of H_2S in biogas occurred for different combined pretreatment conditions. Sludge solubilization achieved due to the mechanical pretreatment increased total cumulative methane production by 8–10% after 30 days during the biochemical methane potential (BMP) test. The pretreatment also improved dewaterability in terms of time to filter (TTF), and decreased methyl mercaptan generation potential of the digested sludge.

1. Introduction

Anaerobic digestion of waste activated sludge (WAS) is difficult compared to primary sludge due to the rate limiting cell hydrolysis step (Pavlostathis and Gosset, 1986). Various techniques including chemical, thermal, and mechanical pre-treatments have been reported in literature for sludge solubilization through cell disruption and making the organic matters available for microbial consumption. Among various chemical treatments, although iron salts and hydrogen peroxide have been used for sludge pretreatment previously, their impacts on anaerobic digestion remain controversial producing conflicting results. For example, while Eskicioglu et al. (2008) have reported 25% reduction in methane yield for thickened WAS treated with hydrogen peroxide (H_2O_2), Rivero et al. (2006) have observed a slight enhancement in biogas production for H_2O_2 treated sludge. Different studies have reported poor digestibility for iron dosed sludge (Smith and Carliell-Marquet, 2008; Ghyoot and Verstraete, 1997; Jack et al., 1976). On the other hand, Lee and Shoda (2008) have reported that iron rich sludge can enhance anaerobic digestion. Although the combination of H_2O_2 and iron salts (also known as Fenton's reagent) has shown significant positive impact on sludge solubilization as well as anaerobic digestion (Erden and Filibeli, 2010), the wastewater to be treated must be acidic (pH 3.00–5.00), and therefore, the pH of pretreated wastewater must be adjusted to the optimum pH of 6.5–7.5 before anaerobic digestion.

Mechanical pretreatment of sludge to enhance hydrolysis rate is based on the microbial cell disruption by shear stresses. Commonly used mechanical pretreatment techniques are ultrasound, mechanical jet, high pressure homogenizer, mechanical ball mill, etc. (Nah et al., 2000; Baier and Schmidheiny, 1997; Tiehm et al., 2001). Although different mechanical pretreatments have shown significant impact on biogas production enhancement, the major challenge of using mechanical pretreatment is high energy requirement. For example, Microsludge™ uses 12,000 psi pressure to solubilize waste activated sludge (Stephenson et al., 2005).

The production of volatile sulfur compounds (VSCs) such as hydrogen sulfide (H_2S), mercaptans, etc. with low odor threshold concentrations is considered as the major reason behind the nuisance odors in anaerobically digested sludges. Hydrogen sulfide (H_2S) in biogas is also undesirable, as it is a very toxic and corrosive gas. Physical and chemical processes used for removal of H_2S from biogas are very expensive (Ahammad et al., 2008). The common VSCs detected in sludge are hydrogen sulfide (H_2S), methyl mercaptan or methanethiol (MT), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS) (ASCE, 1995). Recent studies have shown that the degradation of protein containing amino acids such as cysteine, methionine is closely related to the production of VSCs (Higgins et al., 2004). Lipids (fat, oil and grease) in sludge are also known as responsible for odor generation (Shin-Ichi et al., 1991). Based on the extensive literature search, it can be concluded that the majority of pretreatment studies focused primarily on sludge solubilization

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Nomenclature

ANOVA	analysis of variance
C	amount of substrate (mg COD/L)
F/M	food to microorganism ratio (mg of $COD_{substrate}$/mg of $VSS_{anaerobic\ seed}$)
K	anaerobic degradation rate constant (day^{-1})
LSD	least significant difference
L_u	ultimate biodegradable substrate (mg of COD/L)
r_{su}	substrate utilization rate of anaerobic digester (mg COD/L-d)
S^{2-}	dissolved sulfide (mg/L)
S^{2-}–S	sulfur as dissolved Sulfide (mol)
SBOD	soluble biochemical oxygen demand (mg/L)
SCOD	soluble oxygen demand (mg/L)
SO_4^{2-}	dissolved sulfate (mg/L)
SO_4^{2-}S	Sulfur as dissolved Sulfate (mol)
T	digestion time (day)
TBOD	total biochemical oxygen demand (mg/L)
TCOD	total chemical oxygen demand (mg/L)
Total-S	total sulfur (mol)
TSS	total suspended solids (mg/L)
TTF	time-to-filter (s)
VFA	volatile fatty acid (mg/L)
VSS	volatile suspended solids (mg/L)
Y_t	amount of substrate removed at time t (mg of COD/L)

and enhancement of anaerobic digestibility, and very little effort has gone to the fate of odor precursors and VSCs under pretreatment.

In light of the above literature, this study attempts to systematically and comprehensively evaluate the impact of pretreatment on WAS prior to anaerobic digestion using a laboratory scale system combining mechanical and chemical (H_2O_2 and iron salt) pretreatments. The efficiency of different pretreatment conditions is evaluated in terms of (a) sludge solubilization, (b) biogas production by biochemical methane potential (BMP) test, (c) impact on different odor precursors such as dissolved sulfide, bound protein, and lipid after pretreatment, (d) H_2S control in biogas, and mercaptan generation potential of digested sludge, and (f) dewaterability of digested sludge.

2. Methods

2.1. Waste activated sludge (WAS)

Waste activated sludge (WAS) samples for this study were collected from the Adelaide Pollution Control Plant located in London, Ontario, Canada. After thickening, the sludge was stored in a cold room at 4 °C. The characteristics of the WAS were analyzed before the experiments and are presented in Table 1.

2.2. Pretreatment conditions

The pretreatment of waste activated sludge was done using a laboratory scale sludge pretreatment reactor of volume 12 L. For mechanical pretreatment (MP), 10 L of sludge was pumped from sludge feed tank to the pretreatment reactor using a metering pump (LMI Milton Roy, Model A151-192C, Liquid Metronics Inc., MA 01720 USA) until the pressure of the reactor reached 75 ± 1 psi. The time required to reach 75 ± 1 psi pressure was 20 min. Then after 30 min residence time the pressure of the sludge was released to atmospheric pressure (14.7 psi) through the sludge depressurization valve.

For combined pretreatment (CP), different dosages of hydrogen peroxide (H_2O_2) and iron salts were used. Hydrogen peroxide was added as 50 wt.% H_2O_2 (HX0630-1, EMD Chemicals Inc., Germany), and iron was added as Fe(II) Chloride (98% purity, Sigma Aldrich, Oakville, ON, Canada). The dosages were used based on theoretical requirement of the chemical dosages for dissolved sulfide (S^{2-}) removal in untreated sludge. The theoretical requirements of H_2O_2 and $FeCl_2$ to remove 1 mg dissolved sulfide (S^{2-}) are 0.6 and 1.5 mg, respectively (Walton et al., 2003). Chemicals were added to the sludge feed tank and allowed to mix for 30 min. After mixing, the chemically pretreated sludge was pumped to the pretreatment reactor for mechanical pretreatment. For this study, a total of seven sets of experiments were carried out, each with duplicates. Different pretreatment conditions are summarized in Table 2.

2.3. Biochemical methane potential (BMP) test

To assess the effect of different pretreatment conditions on anaerobic digestibility, the treated waste activated sludge was used for biochemical methane potential (BMP) tests using 300 mL serum bottles. Anaerobic digested seed was collected from the St. Marys wastewater treatment plant, Ontario, Canada. The TCOD, SCOD, TSS and VSS concentrations of anaerobic seed were 16,540, 1742, 12,350, and 9455 mg/L, respectively. The volumes of WAS (substrate) and anaerobic seed based on initial food (COD of substrate) to microorganism (VSS of seed) ratio (F/M) of 2 (mg of $COD_{substrate}$/mg of $VSS_{anaerobic\ seed}$), were 140 and 110 mL, respectively. For the control, the treated WAS (substrate) was

Table 1
Characteristics of WAS.

Parameter	Concentration ($A \pm B$)
TCOD (mg/L)	14,705 ± 123
SCOD (mg/L)	917 ± 22
TBOD (mg/L)	3819 ± 81
SBOD (mg/L)	451 ± 24
TSS (mg/L)	11,880 ± 56
VSS (mg/L)	8730 ± 156
Total VFA[a] (as mg COD/L)	92 ± 3
Lipid (mg/L)	195 ± 7
Dissolved Sulfide (mg/L)	17.5
Total Protein (mg/L)	1174 ± 16
Bound Protein (mg/L)	498 ± 1.79
Soluble Protein (mg/L)	84.5 ± 2.98
Sulfate (mg/L)	20.84 ± 0.46
Ammonia (mg/L)	68 ± 2
Total Nitrogen (mg/L)	1126 ± 26
pH	6.1–6.26
Alkalinity (mg/Las $CaCO_3$)	767 ± 19

A = Arithmetic mean of duplicate measurement.
B = Absolute difference between mean and duplicate measurement.
[a] Summation of acetic acid, propionic, butyric, iso-butyric, valeric, and isovaleric acids.

Table 2
Summary of pretreatment conditions.

Set	Chemical dosages	
	mg of H_2O_2/mg dissolved S^{2-}	mg of $FeCl_2$/mg dissolved S^{2-}
Control	–	–
MP	–	–
CP 1	0.6	1.5
CP 2	1.5	1.5
CP 3	0.6	3
CP 4	1.5	2.5
CP 5	2	2.5
CP 6	2	3