International Journal of Civil and Structural Engineering Research ISSN 2348-7607 (Online)
Vol. 7, Issue 1, pp: (129-133), Month: April 2019 - September 2019, Available at: www.researchpublish.com

VS destruction and its impact on VOSC generation under thermophilic and mesophilic anaerobic digestion conditions

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Abstract: **Greater organic removal may result in less odorous sludge cake. Thermophilic (55℃) anaerobic digestion (TAD) and mesophilic (37℃) anaerobic digestion (MAD) were tested to understand if greater volatile solids reduction (VSR) could be related to less sulfur-based organic odor or volatile organic sulfur compounds (VOSCs) generation from dewatered and digested sludge. The TAD system removed 10% additional VS than the MAD system, which was reconfirmed by soluble and extractable biopolymer data. The TAD system held more soluble biopolymer than the MAD system while less extractable biopolymer was observed from TAD than MAD. However, greater organic solids removal did not result in lower odor in biopolymer cakes. Hydrogenotrophic methane formers might be responsible for less VOSC removal from thermophilically digested and dewatered sludge.**

Keywords: **Thermophilic anaerobic digestion, mesophilic anaerobic digestion, organic solid reduction, volatile organic sulfur compound.**

I. INTRODUCTION

Under high temperature (50-60℃) conditions, TADs are able to utilize higher kinetic energy resulting in enhanced solid reduction [15] and better pathogen control than conventional MADs (35-37℃). However, the TAD tends to cause the digestion instability due to high volatile fatty acid production and high ammonia generation due to enhanced protein degradation [8].

Organic sulfur compounds, which are responsible for odors from most dewatered sludge cakes, are generated by complex transformation processes. As described by Higgins et al. [6], volatile organic sulfur compounds (VOSCs) can be produced from anaerobically digested sludge by the degradation of sulfur-containing amino acids such as cysteine and methionine, which can be converted to hydrogen sulfide (H_2S) and methanethiol (MT), respectively. Methylation of sulfide and MT by transferring a methyl group from methoxylated aromatic groups like syringate and 3,4,5-trimethoxybenzoate is also suggested as a pathway of MT and Dimethyl sulfide (DMS) generation in anaerobic environments [9]. Dimethyl disulfide (DMDS) can be generated by the oxidation of MT [9].

It has been known that methylotrophic methanogens are responsible for VOSC degradation. Sulfide, methane and carbon dioxide are the final products of mineralization of VOSCs by these methanogens. However, sulfate reducers also have shown anaerobic degradation of MT and DMS [9], [13]. Tanimoto and Bak [13] reported that sulfate reducers from a thermophilic fermenter sludge degraded MT and DMS to carbon dioxide and sulfide with sulfate as an electron acceptor. High sulfide or sulfate environments are likely to stimulate sulfate reducers to outcompete methanogens for VOSC uptake in the freshwater sediments [9].

In this study, two batch anaerobic digestion systems (TAD and MAD) were operated to study their ability to reduce solids and VOSCs. The objectives of this study were;

a) To compare the solid reduction efficiencies of the TAD and the MAD;

b) To compare the VOSC reduction potentials of the TAD and the MAD; and

c) To search for the way to link solid reduction to VOSC generation.

II. METHODOLOGY

The TAD and MAD reactors were prepared with a HDPE laboratory water container. This anaerobic digester was covered with aluminum foil, on which a temperature adjustable heating tape was applied. The temperature of the TAD was maintained at 55℃ and the MAD was operated at 37℃. Sludge retention time of each reactor was 24 days. The operational volume of both reactors was 12L. Feed sludge was prepared by mixing thickened waste activated sludge (TWAS, 5% TSavg) shipped from the WLSSD wastewater treatment plant at Duluth, MN and tap water to make a 3% total solid (TS) feed. There is no primary treatment practiced in the WLSSD. Mechanical mixing by a stirring plate and bar was applied to the reactor. A gas collecting bag was installed to the top of the reactor to reduce excess gas pressure.

Total and volatile solids (TS/VS), total Kjeldahl nitrogen (TKN) and ammonia nitrogen were measured in accordance with standard methods [1].

Total cations (Na, Ca, Mg, Al and Fe) in the sludge samples were measured using U.S. Environmental Protection Agency Method 3050B [14]. A well-mixed liquid sludge was treated with acid digestion and each cation species was quantified by atomic absorption spectroscopy (AAS).

The method developed by Dubois et al. [3] was applied to quantify solubilized polysaccharide with dextrose as a standard. The concentration of solubilized protein was measured by the method of Frølund et al. [4]. Bovine serum albumin (BSA) was used as a standard.

The cation exchange resin (CER) and base extraction methods were applied to sludge samples to release solid-bound exocellular polymeric substances (EPS) into the solution as described by Park and Novak [12]. Mechanical shear was also applied to sludge samples to extract EPS that is susceptible to shearing. One hundred ml of sludge sample was centrifuged for 15 minutes at 15000 rpm under 4℃ and the pellet was resuspended in a phosphate buffer solution (PBS) with the final volume of 200 ml. The resuspended sludge was subjected to 1-minute shearing, 1-minute rest and 1-minute reshearing followed by centrifugation for 15 minutes at 10000 rpm under 4℃. The supernatant was filtered through 0.45 μm membrane filter and the filtrate was stored in a -20℃ freezer for the biopolymer measurement.

Sludge dewaterability was tested by applying the method devised by Muller et al. [10]. One % Clarifloc (C3268, Polydyne Inc.) solution was used as a sludge conditioner and the optimum polymer dose was determined as a polymer dose that gave the lowest capillary suction time (CST).

Odor was quantified by the method described by Glindemann et al. [5]. The pressed sludge pellet was incubated in a glass bottle sealed with Teflon lined septa.

III. RESULT AND DISCUSSION

The TAD showed greater volatile solid (VS) reduction than the MAD (41% vs. 32%). Gas production data confirmed the greater solid reduction capability of the TAD than the MAD (Data is not provided here.). Higher solid reduction resulted in greater soluble biopolymer release into the TAD system while less solution biopolymer was observed from the MAD system (TABLE I).

TABLE I. SOLUBLE BIOPOLYMER IN TAD AND MAD

	TAD		MAD	
	Concentration (mg/l)	% change from feed	Concentration (mg/l)	% change from feed
Polysaccharide	180±34	+17	65±19	-66
Protein	182±103	+32	75±15	-11

The greater amount of solution biopolymer release from the TAD necessitated higher polymer dose for dewatering processes and caused poorer dewatering, which are evidenced by a higher CST (TABLE I and II). Novak and Park [11] also suggested a proportional relationship among solution biopolymer content, sludge conditioner requirement and sludge dewaterability.

TABLE II. SLUDGE CONDITIONING

	Optimum Polymer (mg/g TS, avg)	Raw sludge CST (sec)
TAD	42	4576
MAD	23	292

*TAD: Thermophilic anaerobic digestion; MAD: Mesophilic anaerobic digestion

** Cationic polymer (Clarifloc, 1%) was used for conditioning of sludge.

Solid bound biopolymer profile was also collected to view the reduction of EPSs of sludge samples before and after the TAD and MAD system. The percent removal data of CER and base extractable biopolymer in the TAD and the MAD are given in TABLE III. CER appears to extract divalent (Ca^{2+} and Mg^{2+})-bound biopolymer from the sludge samples while base extraction seems to release multi-valent cation (e.g. Al^{3+}) -bound biopolymer into the solution [12]. Considering that divalent cations were the most abundant among the cation species in the TAD and the MAD (Data is not provided here), CER extractables may be a good representative of the extractable biopolymer profile for this study. The high temperature anaerobic digestion provides greater percent removal of cation-bound biopolymer. In addition, high temperature seems to enhance removal of multi-valent cation (e.g. Al^{3+}) - bound biopolymer.

TABLE III. EXTRACTABLE BIOPOLYMER

	% reduction of ***CER*** extractable biopolymer from the feed sludge		% reduction of ***Base*** extractable biopolymer from the feed sludge	
	Protein	Polysaccharide	Protein	Polysaccharide
TAD	56	46	71	79
MAD	31	49	28	52

However, the concentrations of biopolymer released by mechanical shear increased as sludge went through both TAD and MAD (Fig.1). It appears that mechanical shear releases biopolymer from the sludge that was not degraded during the TAD and MAD.

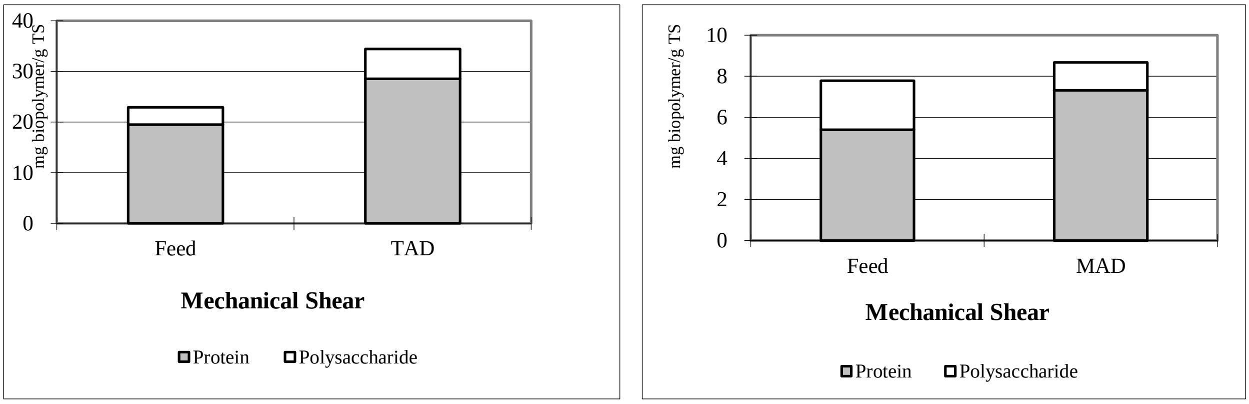

Figure 1. Mechanical shear extractable biopolymer profile of the TAD and the MAD.

Odors generated from sludge cakes are tabulated in TABLE VI. The TAD produced much more odors than the MAD. The peak TVOSC generated from the TAD was about 60 times greater than those from the MAD. In addition, the peak volatile sulfur compounds from the TAD appeared at a much later incubation time than from the MAD.

TABLE IV. ODOR TEST RESULTS

	Peak TVSC (ppmv as S/g VS)	Incubation days till peak TVSC	Peak TVOSC (ppmv as S/g VS)	Incubation days till peak TVOSC
TAD	4265 ± 1531	24 ± 2	293 ± 63	22 ± 14
MAD	2527 ± 486	8 ± 5	5 ± 3	9 ± 4

* TVSC includes TVOSC and hydrogen sulfide.

Considering the greater VS reduction, less VOSC generation was expected from the TAD. However, TVOSC generated from the TAD was much greater than the MAD. Colleran and Pender [2] reported that acetoclastic methanogens are the major acetate consuming microbes in the MAD system with (COD to sulfate ratio near 4) or without sulfate while sulfate reducing bacteria (SRB) outcompete hydrogenotrophic methanogens for hydrogen. On the other hand, hydrogenotrophic methanogens were dominant in the TAD system. It can be speculated that acetoclastic methanogens, some of which were reported as VOSC degraders [9], converted VOSCs to hydrogen sulfide and methane with the help of hydrogenotrophic SRBs in the MAD system. However, acetoclastic methanogens may not be dominant in the TAD system due to the high sulfate which leads to higher SRB while hydrogenotrophic methanogens, which are less likely to mineralize VOSCs, appeared to take charge of the system. This speculation can be supported by the VFA data with near complete removal of acetate from the MAD and only 62% acetate removal from the TAD.

A study is going on in the Virginia Tech to elucidate the mechanisms of VOSC generation in association with enhanced solid removal processes. Future studies will include VOSC removal of sulfate reducing bacteria in different anaerobic sludge digestion conditions.

IV. CONCLUSION

1. The TAD showed greater solid reduction than MAD, which was supported by higher biopolymer release and enhanced removal of cation-bound biopolymer by the TAD.
2. Although the TAD removed more solids than the MAD, it was the MAD that generated less VOSCs, which were thought to be the product by the degradation of sulfur-containing amino acids.
3. It appears that higher solid reduction does not always ensure less VOSC generation from the dewatered sludge cakes. Other conditions such as sulfate in the influent, different microbial community, etc. may be involved.

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