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Effects of metal salt addition on odor and process stability during the anaerobic digestion of municipal waste sludge

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ABSTRACT

Anaerobic digestion (AD) is an effective way to recover energy and nutrients from organic waste; however, several issues including the solubilization of bound nutrients and the production of corrosive, highly odorous and toxic volatile sulfur compounds (VSCs) in AD biogas can limit its wider adoption. This study explored the effects of adding two different doses of ferric chloride, aluminum sulfate and magnesium hydroxide directly to the feed of complete mix semi-continuously fed mesophilic ADs on eight of the most odorous VSCs in AD biogas at three different organic loading rates (OLR). Ferric chloride was shown to be extremely effective in reducing VSCs by up to 87%, aluminum sulfate had the opposite effect and increased VSC levels by up to 920%, while magnesium hydroxide was not shown to have any significant impact. Ferric chloride, aluminum sulfate and magnesium hydroxide were effective in reducing the concentration of orthophosphate in AD effluent although both levels of alum addition caused digester failure at elevated OLRs. Extensive foaming was observed within the magnesium hydroxide dosed digesters, particularly at higher doses and high OLRs. Certain metal salt additions may be a valuable tool in overcoming barriers to AD and to meet regulatory targets.

1. Introduction

Anaerobic digestion (AD) is one of the most effective methods of stabilizing the solid residuals from municipal wastewater treatment as it converts organic matter into valuable by-products including a methane-rich biogas and a nutrient-dense digestate which is ideal for composing or land application. AD has many benefits; however, issues like odorous and corrosive gases in AD biogas, and the release of nutrients during the digestion of biological nutrient removal (BNR) sludge back into the liquid stream can limit the wider adoption of AD.

High levels of corrosive and odorous gasses are generated during AD which can damage biogas handling and utilization equipment and can greatly effect nearby residents. Volatile sulfur compounds (VSCs) have been reported as the most problematic odorous compounds produced during AD due to their high concentrations in AD biogas (500–3000 ppmv) and the ability of people to detect them at very low levels (<0.100 ppmv) (Soroushian et al., 2006; Sanin et al., 2010). VSCs include hydrogen sulfide (H_2S) and a number of other volatile organic sulfur compounds (VOSCs) including methyl mercaptan (MM), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), etc. In addition to odors and toxic effects, VSCs can be damaging to plant infrastructure including concrete, piping, process and biogas utilization equipment (Du and Parker, 2009a).

Existing literature has also shown that many odorous sulfur-based compounds are produced when bioavailable proteins are degraded (Adams et al., 2003; Chen et al., 2005; Higgins et al., 2006), while the production of H_2S and MM in anaerobic environments from the decomposition of the amino acids, such as cysteine and methionine has been well established (Persson, 1992; Persson et al., 1990; Yoshimura et al., 2000). Another significant VSC precursor is sulfate (SO_4^{2-}) which plays a significant part of the sulfur cycle (Water Environment Federation, 2008). Oremland and Taylor (1978) demonstrated that sulfate reducing bacteria (SRB) produce H_2S from the reduction of various forms of inorganic sulfur like sulfate.

Once H_2S and MM are produced, various mechanisms can transform H_2S and MM into other VOSCs. Numerous studies have explored the fate of VOSCs in biosolid storage areas and batch digestion as H_2S and VOSC concentrations change rapidly within the first hours of storage/digestion and continue changing for many days afterward. Methanogenic bacteria have been shown to degrade VOSCs into intermediate products and H_2S under anaerobic conditions, particularly in low sulfate conditions (Chen et al., 2005; Du and Parker, 2009a; Van Leerdam et al., 2008). The

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transformation of VOSCs into H_2S helps to explain the low levels of VOSCs present in AD biogas (when compared to H_2S).

While extensive research has been conducted on biosolids and odors, most studies have explored odor from dewatered biosolids by batch testing in small serum bottles, or odor levels in facilities that handle, store or process biosolids. Very little research has been done to identify and /or quantify the odorous compounds present in the biogas of continuously-fed complete mixed AD, while even less has been done on techniques to reduce or to prevent their formation. Sludge cake, batch, and serum bottle testing conducted by Higgins (2010) and Novak and Park (2010b) have explored the impact of iron and aluminum concentrations present and added showed great promise and an opportunity for further study. These studies and other available literature suggest that it may be possible to significantly reduce VSCs production with AD by adding certain metal ions into the digester feed.

Another issue with AD is the solubilization (release of materials from the solid phase into the liquid phase) of biologically bound nutrients when sludge from a BNR process is digested. Significant amounts of phosphorous (as orthophosphate) and ammonia can be released during digestion and dewatering of the digested sludge (Pitman et al., 1991) which can cause effluent nutrient levels that exceed discharge limits for wastewater treatment plants (WWTPs) with BNR process as the liquid from the dewatered sludge (centrate) is returned to the beginning of the WWTP for treatment.

The authors of this paper propose a hypothesis that the addition of iron, aluminum and magnesium salts commonly used in sewers and wastewater treatment facilities for odor control or chemical precipitation of other pollutants will have an effect on the production of highly odorous VSCs in AD headspace biogas and can impact AD performance and stability. Existing literature has shown a strong correlation between iron and aluminum concentrations in AD sludge and the production of VSCs from dewatered sludge cake (Higgins, 2010; Novak and Park, 2010b). Magnesium hydroxide is highly alkaline and may shift the balance between H_2S in the gas phase and bisulfide (HS^-) to the soluble HS^- form in the liquid phase of the digester (Jefferson et al., 2002). To validate this hypothesis, this study explored the effects of adding two concentrations of three different metal salts to AD feed immediately before digestion on digester headspace VSCs, digester stability and digestate orthophosphate concentrations.

2. Materials and methods

2.1. Experimental design

The effects of adding metal salts to the feed of semi-continuously fed bench-scale ADs were explored in a two-stage experiment conducted at the Bioreactor Technology Research Laboratory at the University of British Columbia. Stage one employed two different metal salts added to two of three ADs (the third one was not dosed, and served as "control"), while stage two employed two different doses of three metal salts added to four of five ADs (the fifth digester was control) as shown in Fig. 1.

Ferric chloride, aluminum sulfate, and magnesium hydroxide were selected as the metal salts due to their low cost and widespread use in sewers and existing WWTPs. Furthermore, iron, aluminum and magnesium were chosen as the metals of study as levels of these metals in compost and biosolids are not regulated by the United States Environmental Protection Agency (EPA) nor by most other regulatory agencies. Thus, elevated levels of these metals would not negatively affect the beneficial re-use of these materials in agriculture. Total iron and aluminum concentrations were selected based on the results of the Water Environment Research Foundation Report *Evaluation of Aluminum and Iron Addition during Conditioning and Dewatering for Odor Control* (Report 03-CTS-9B). This study demonstrated that higher levels of iron and/or aluminum in batch-digested sludge had an inverse effect on VSC production from the resulting sludge cake (Novak and Park, 2010b). Total magnesium concentrations were selected based on levels of magnesium hydroxide that had been shown to improve sludge digestibility and dewaterability according to Wu et al. (2001) and Wu et al. (2005).

Stage one increased the total levels of iron to 7.40 mg of iron per gram of total solids (TS) in feed sludge by adding powdered ferric chloride hexahydrate (97–102% $FeCl_3 \cdot 6H_2O$), or total levels of aluminum to 10.74 mg of aluminum per gram of TS in the feed sludge of the other dosed digester by the addition of a liquid aluminum sulfate solution (49% by mass $Al_2(SO_4)_3 \cdot 14H_2O$). Stage two employed a higher level of each metal ion of either 9.43 mg of iron per gram of TS, or 14.31 mg of aluminum per gram of TS. Stage two also included two additional digesters in which a total of either 4.89 or 5.27 mg of magnesium per gram of TS was achieved by the addition of a magnesium hydroxide solution. All compounds during both stages were added directly to the undigested sludge immediately before feeding. In both stages, "control" digesters represented a conventional AD operation to use for comparison. Existing (baseline) metal concentrations in the raw sludge were determined by an external laboratory which prepared the samples according to EPA method 3050B (Acid Digestion of Sediments, Sludges, and Soils) which were then analyzed by inductively coupled plasma-mass spectrometry (ICP-MS).

American Chemical Society (ACS) grade (97–102%) ferric chloride hexahydrate was purchased from Fisher Scientific (Ottawa, Ontario); a solution of 49% aluminum sulfate was acquired from Cleartech Chemicals (Saskatoon, Saskatchewan); while reagent grade (95%) magnesium hydroxide was purchased from Sigma–Aldrich (Oakville, Ontario). The aluminum sulfate solution was used as-is while the magnesium hydroxide solution was prepared by adding 3.00 g of reagent grade (95%) $Mg(OH)_2$ powder to one liter of ultra-pure water.

2.2. Anaerobic digester configuration

Eight semi-continuously fed bench-scale mesophilic (35 °C) ADs were run over a one-year period in two overlapping stages. Each AD was constructed out of a 1.5-L glass erlenmeyer flask, and was sealed with a rubber stopper and silicone sealant. Hollow glass tubes were inserted through the stoppers for collection of digested sludge and headspace biogas in 2-L Tedlar® bags while the digester was fed via the sidearm of the flask. When not being fed, the flasks were incubated at 35 ± 0.1 °C in a temperature controlled shaker at 80 rpm to simulate the conditions inside a full-scale, complete mix-reactor. Each digester was fed and wasted once daily (including weekends and holidays) and was swirled immediately before the removal of digested sludge to prevent settling of solids within the digester and to allow for the collection of representative samples.

2.3. Inoculum and digester operation

Inoculum was obtained from an existing automated fermenter operating at the same laboratory. This digester has been operating as a continuous-flow, mesophilic (35 ± 2 °C) AD with a sludge retention time (SRT) of approximately 20 days since January 2012 and had originally been seeded with effluent from a full-scale AD operating at a WWTP in a nearby community (Penticton, B.C.). The automated AD utilized the same feed sludge used for this study and was well acclimatized to it.