The Effect of Cations on Volatile Solids Destruction, Odors, and Dewatering in anaerobic digestion

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ABSTRACT

The primary purpose of this study is to understand the effects of wastewater sludge feed cations on volatile solids destruction, odor control, and dewaterability. The role of influent feed cations and addition of chemical coagulants to sludge were evaluated for those characteristics following anaerobic digestion. Wastewater sludge samples were obtained from seven municipal wastewater treatment plants. Subsequently, batch digestion of the sludges was performed anaerobically in the laboratory with 30 days of SRT. Conditioning with cationic polymer and dewatering simulating a high solids centrifuge were performed after digestion. It was found that volatile solids destruction and volatile organic sulfur compounds generation increased proportionally as iron content in influent increased. However, they decreased as aluminum content in influent increased. It was also found that as iron content in influent increased, higher optimum polymer dose was required for dewatering. On the contrary, increase in aluminum content in influent resulted in decrease in the amount of optimum polymer dose. Direct addition of iron to the digesting sludge can be the most efficient point of addition with respect to volatile solids destruction, odor control, and conditioning of digested sludge.

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Introduction

Digestion is a biological process commonly used for the stabilization of sludge from wastewater treatment plants such as destruction of pathogens and reduction in both volatile solids (VS) and volatile organic sulfur compounds (VOSCs) (Novak *et al.*, 2003). Cations, especially metals and metal-associated sludge in the digester may be important factors for prediction of the digestion performance such as solids destruction and odor generation. Basically, it is difficult to predict digestability and effluent sludge characteristics only with the information of process used. Such prediction is of importance and cost-effective when the design of wastewater treatment is made and consulted (Novak *et al.*, 2007). In order to understand the effect of cations on anaerobic digestion, the role of cations in floc structure should be preceded. Park and Novak (2007) has proposed that there should be iron bound organics that could be degraded by anaerobic digestion, aluminum bound fraction that has resistant characteristics against biological degradation under aerobic and anaerobic condition, and divalent such as calcium and magnesium bound fraction that could be degraded only by aerobic digestion. Novak *et al.* (2003) also studied that flocs associated with iron or Ca^{++} and Mg^{++} in the activated sludge are digested differently.

Recently, Park *et al.* (2006) found that volatile solids destruction of the activated sludge under anaerobic condition is dependent on the iron content in the sludge. This result enables to study odor generation according to metals in sludge under anaerobic condition in

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company with digestability. Murthy *et al*. (2000) suggested that iron in sludge has an affinity on protein. Iron in sludge is reduced when it exists in an anaerobic digester and the organics associated with iron are released in combination with sulfide. These released organics but not all can be degraded in the digester, resulting in the volatile solids destruction. As an increase in iron in sludge, volatile solids destruction increases (Novak *et al*. 2007). In addition, VOSCs from the dewatered sludge cake also increase in spite of increase in volatile solids destruction with increase in iron content in sludge. It is thought that odors are generated by further release of protein that has remained undegraded in the digester through shear when iron exists. However, Novak *et al*. (2002) found that Ca^{++} and Mg^{++} associated organics are not related to odor generation from the dewatered sludge cake since Ca^{++} and Mg^{++} are not increased after centrifugation.

Anaerobically digested sludge that is not inhibited for VOSC degradation has generally low odors. However, dewatering process can cause the disturbance of balance between production and degradation rate of VOSC, thereby increasing odors significantly. This occasion would be categorized as dewatering equipment, polymer dose, and cake handling and transport (Higgins *et al.*, 2006). Firstly, high-solids centrifuges trigger not only more exposure to the air that leads to inhibit the activity of methanogens that play a role in degrading VOSCs, but also imparting more shear causing cell lysis and damage or greater floc breakup, resulting in increase in odors. Odors associated with biosolids resulted from high-solids centrifuges are usually more produced than medium-solids centrifuges which are greater than belt-filter presses (Murthy *et al.*, 2003). Secondly, increase in polymer dose promotes isolation of soluble protein present in liquid sludge depositing the protein into the

cake sludge. Thus, the increased amount of protein which is bioavailable as a substrate for the production of VOSCs could result in more odor production during storage (Higgins *et al.*, 2002, Murthy *et al.*, 2003). Lastly, transport of cake through high-shear conveyance such as cake pumps and screw conveyors could likely raise the odor production (Murthy *et al.*, 2002). Therefore, further study regarding the effect of feed cations and their point of addition on volatile solids destruction and odor production is necessary to better operate and design wastewater plants for managing biosolids and controlling odor problems. Dewatering is one of the important drying processes since a lower volume of sludge results in cost-effective application. Chemicals are usually added to improve the efficiency of dewatering processes and the quality of the filtrate or centrate. In a municipal wastewater treatment plant, high-solids centrifuges or belt filter presses are commonly used (Novak, 2006). Dentel (2001) studied the selection of the conditioning chemicals to achieve good dewatering rates using both synthetic organic polymers and metal ions, usually iron salts. These chemicals are normally used for coagulation and removal of the colloidal fractions, aggregating them in the sludge. When the optimal conditioner is used in sludge, water is separated faster (Novak, 2006).

The structure and role of floc determine the dewatering and conditioning requirements of biological sludges (Novak *et al.*, 2001). Higgins and Novak (1997a) proposed that the integral structure of floc mainly consists of biopolymer bound by cations. Poor effluent quality and dewaterability were shown to occur when monovalent cations exceed divalent cations in the wastewater influent. In addition, Higgins and Novak (1997b) showed that the most prominent constituent of floc is the protein component in the biopolymer. A mix of

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proteins, polysaccharides, and humic acids in wastewater appears to be collected by aluminum and iron. The aluminum-associated fraction has been poorly studied. However, it is thought that iron content in the sludge results in the release of biopolymer into solution when iron is reduced. Much of this released biopolymer consists of biocolliods with a size range between 1.5 μm and 30,000 daltons. As more floc protein is released, residual undegraded accumulates in solution. The biopolymer fraction that is released to solution and not degraded results in a higher dose of polymer and poor dewatering (Bivins and Novak, 2001). Thus, polymer dose in sludge is determined by these colloidal proteins that are remained and interfere with dewatering under anaerobic condition. The accumulation of the colloidal material is related to volatile solids destruction. Dewatering properties become poorer as the efficiency of anaerobic digestion increases. According to a related study by Park (2002), conditioning and dewatering properties could be predicted based on the cations content, thereby providing a tool of estimation for sludge handling costs prior to a digestion facility construction.

Nature of Anaerobic Operation

Understanding the multistep nature of anaerobic biochemical operations is of importance since the interaction between the bacteria and the archaea occurs in both suspended and attached growth system. The insoluble organic matter or complex biodegradable particulates are hydrolyzed to proteins, carbohydrates and lipids. Also, the size reduction to facilitate transport across the cell membrane is considered as hydrolysis reactions (Grady *et*

al., 1998).

Amino acids and sugars are degraded to acetic acid by fermentative reactions under anaerobic condition. Volatile and long chain fatty acids are transformed to hydrogen through anaerobic oxidation. Both acetic acid and hydrogen are the direct methane precursors in anaerobic operations. In this acidogenesis system, the high partial pressure of hydrogen could be a thermodynamic inhibitor for the anaerobic oxidation if hydrogen levels exceed certain concentrations (McCarty and Smith, 1986). Acetic acid, H_2, methanol, and methylamines can be used as substrates for methane production (Grady *et al*., 1998).

Methanogens utilize the products of the acidogenesis, acetic acid and H_2, to produce methane gas. Aceticlastic methanogens which are involved in splitting acetic acid into methane and carbon dioxide and H_2-oxidizing methanogens which reduce carbon dioxide participate in this methanogenesis reaction. Generally, two-thirds of methane formation in anaerobic digestion are from acetic acid and the remaining portion is derived from H_2 and carbon dioxide (Grady *et al*., 1998). These methanogens have a relatively low maximum growth rate, so that they are rate-limiting anaerobes which require a relatively long detention time (Metcalf and Eddy, 1991).

The Role of Cations in Anaerobic Digestion

Chemical coagulants such as alum and ferric chloride are commonly used for suspended solids and phosphorus removal in wastewater treatment. Both coagulation and phosphorus removal may be achieved simultaneously when coagulants are applied to the primary or

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secondary treatment processes (EPA, 1975). However, that practice may have adverse effects on biological digestion of the sludge solids bound to coagulants (Rudolfs *et al.*, 1932, Derrington *et al.*, 1973, Brown & Little, 1977, Baillod *et al.*, 1977). Gossett *et al.* (1978) studied the adverse effects on both plant-scale and bench-scale digesters which received coagulants. They found a significant decrease in volatile solids destruction, COD removal, organic nitrogen catabolism, alkalinity production, methane production, and total gas production. However, toxicity resulting from the dosing of alum or ferric chloride is not that significant (Grady *et al.*, 1998). The mechanisms causing reduced degradation are thought to be due to coagulants locking up substrates such as proteins (Rudolfs & Setter, 1931) or phosphate limitation caused by aluminum and iron addition (Pfeffer & White, 1964).

Cations, especially metals and metal-associated sludge may be important factors for prediction of digester performance such as solids destruction and odor generation. Basically, it is difficult to predict digestability and effluent sludge characteristics. Such predictions are of importance when the design of wastewater treatment is made (Novak *et al.*, 2007). In order to understand the effect of cations on anaerobic digestion, the role of cations in floc structure must be understood. Park and Novak (2007) has proposed that there are iron bound organics that are degraded by anaerobic digestion. The aluminum bound fraction has resistant characteristics against biological degradation under aerobic and anaerobic condition, and divalent cations such as calcium and magnesium bind a fraction that can be degraded only by aerobic digestion. Novak *et al.* (2003) also proposed that flocs associated with iron or Ca^{++} and Mg^{++} in the activated sludge digest differently from one another.

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Higgins and Novak (1997a) have shown that cations such as Ca^{++} and Mg^{++} can affect the characteristics of sludge settling and dewatering and the effluent quality from activated sludge.

The Effect of Iron and Aluminum on Digestion and Odors

Recently, Park *et al*. (2006) found that volatile solids destruction of activated sludge under anaerobic condition is dependent on the iron content in the sludge. Murthy *et al*. (2000) suggested that iron in sludge has an affinity for protein. Park *et at* (2006) proposed that iron in sludge is reduced when it enters in an anaerobic digester and the organics associated with iron are released in combination with sulfide. These released organics are degraded in the digester, resulting in volatile solids destruction. As the iron in sludge increases, volatile solids destruction also increases (Novak *et al*., 2007).

As iron increases in sludge, VOSCs from the dewatered cake also increase in spite of an increase in volatile solids destruction (Novak *et al*., 2007). It is thought that odors are generated by the additional release of protein that remains undegraded in the digester. The release results from shear, especially during dewatering. These results conflict with the volatile solids destruction and stability regulation by the Environmental Protection Agency (Novak *et al*., 2007). However, Novak *et al*. (2002) found that Ca^{++} and Mg^{++} associated organics are not related to odor generation from the dewatered sludge cake since Ca^{++} and Mg^{++} do not increase during high shear centrifugation.

In addition, Higgins and Novak (1997b) suggested that the M/D ratio, which indicates

the ratio of monovalent cations to divalent cations, could be associated with dewatering characteristics and settling properties. When the M/D ratio is high, the floc structure becomes weak so that it could be easily broken down by shear. Thus, the hypothesis is that odors would be increased as the M/D ratio increases. However, experimental data has shown that no correlation exits between M/D ratio and odor generation. Also, it was found that odors and aluminum content in sludge are in inverse proportion (Novak *et al.*, 2007). The reason of low odor production when aluminum content is high in sludge is that aluminum associated organics are not likely released from floc by shear. These results could be the foundation for predicting the odor generation in the anaerobic digestion. However, further study is needed to support and clarify the role of iron and aluminum in odor production and digestion (Novak *et al.*, 2007).

Cycling of VOSC Production and Degradation

The balance between the production and degradation of volatile organics sulfur compounds (VOSCs) likely exists in fresh water sediments, resulting in low VOSCs emissions. This means that the production rate of VOSCs is basically equal to the degradation rate of VOSCs under steady-state conditions (Lomans *et al.*, 2001). However, if toxic or inhibitory compounds such as chloroform, toluene, or sodium are added to an anaerobic digester, this balance would be disturbed and the degradation of VOSCs would be delayed, resulting in accumulation of VOSCs (Zitomer and Speece, 1995, Zitomer *et al.*, 2000). Data has shown that methanethiol (MT) is likely to accumulate when methanogenic activity is retarded

(Higgins *et at*., 2006). Thus, an increase in MT in anaerobic digesters could be an indicator of toxicity (Zitomer *et al*., 2000).

Higgins *et al*. (2006) has studied that the production, degradation, and transformation of volatile organic sulfur compounds which follow certain cyclic pathways during cake storage. In the production of odor-causing VOSCs the formation of H_2S and MT result from degradation of protein. In addition, the free sulfate and sulfonate-based surfactants present in wastewaters contribute another source of hydrogen sulfide although the amount may be low (Field *et al*., 1995, Prats *et al*., 1997, Wagener and Schink, 1987, White and Russel, 1995). A strong correlation between the peak MT concentration measured during incubation of sludge cakes and the mass of bound methionine extracted from biosolids cake has been shown for 10 different mesophilic anaerobically digested sludges. The peak concentration of MT increased linearly as the mass of bound methionine increased (Higgins *et al*., 2004).

The generation of MT and dimethyl sulfide (DMS), appears to be from methylation of H_2S and MT in which methyl groups are added to them (Higgins *et al*., 2006). The degradation of methionine or cysteine results in the formation of DMS.

Dimethyl disulfide (DMDS) is readily formed from oxidation of methanethiol when oxygen is present in the environment (Chin and Lindsay, 1994, Fritz and Bachofen, 2000, Kelly and Smith, 1990, Parliament *et al*., 1982, Tulio *et al*., 2002). Lehninger *et al*. (1993) has suggested that the thiol groups in cysteine readily form disulfide bonds through oxidation of the protein which can be catalyzed by agents such as iron and copper (Chin and Lindsay, 1994, Prentice and Bryce, 1998). This fact corresponds with the result of

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Higgins *et al*. (2006) that MT was produced only after DMDS reached its peak and started to decrease. Also, additional research data support the fact that the formation of DMDS from MT only occurrs when oxygen is present. It has been observed that the concentration of MT increased, and DMDS formation stopped when the oxygen is exhausted in the serum bottle (Higgins *et al*., 2006).

Controlling of VOSCs

Recent surveys have shown that nuisance odors associated with biosolids are highly ranked as the top concern and are the main restriction for land application programs (Adams *et al*., 2003, Dixon and Filed, 2004). Thus, reducing odors associated with biosolids has significant importance for land application as a low-cost disposal method for biosolids, a low-cost nutrient source, and a soil amendment for farmers (Higgins *et al.*, 2006). Higgins *et al*. (2006) suggested two possible strategies in order to control volatile organic sulfur compounds. The first method could be removal of precursors for VOSCs generation. Protein is the parent material for cysteine and methionine, the odor causing amino acids. Also, intermediate reactions such as demethylation would aid in decreasing VOSCs-related odors. Removal of hydrogen sulfide that is the final product of demethylation would help prevent the production and degradation cycle of VOSCs from proceeding further. Changes in digestion operations, dewatering processes, storage and land application methods, and chemical addition to biosolids before and after dewatering may also be useful control methods for reducing odors. When better digestion performance is achieved, the protein

concentration could be reduced, thereby decreasing in the amount of substrate for production of odorous VOSCs. Secondly, methanogenic activity could be increased. This could be done by reducing inhibition of methanogens by chemical adjustment or reducing sludge to oxygen exposure which occurs in a centrifuge (Muller and Novak, 2008).

Relationship between Dewatering and Biosolid Odors

Odors associated with anaerobically digested sludge cake are important for dewatering, transport, and land application with regard to esthetic effects and potential health risks (Novak *et al.*, 2006). Anaerobic digestion for land application is commonly used in order to reduce odors and vector attraction. However, dewatering process associated with anaerobically digested sludge may lead to unacceptable odors (Murthy *et al*., 2002). This is especially true for high-solids (high shear) centrifuges.

Anaerobically digested sludge that does not inhibit VOSCs degradation has relatively low odors. However, dewatering process can cause the disturbance of the balance between production and degradation rate of VOSCs, thereby significantly increasing odors. Factors that lead to this disturbance may be categorized as dewatering equipment, polymer dose, and cake handling and transport (Higgins *et al.*, 2006).

First, high-solids centrifuges trigger more exposure to the air that leads to inhibition of the activity of methanogens that play a role in degrading VOSCs. Centrifuges may also impart shear causing cell lysis or floc breakup, resulting in protein degradation and an

increase in odors. Odors associated with biosolids resulting from high-solids centrifuges are usually greater than from medium-solids centrifuges which are, in turn, greater than belt-filter presses (Murthy *et al.*, 2003).

Second, an increase in polymer dose promotes isolation of soluble protein present in liquid sludge and stimulates to deposit the protein into the cake sludge. This appears to increase the amount of protein which is bioavailable as a substrate for the production of VOSCs and result in more odor production during storage (Higgins *et al.*, 2002, Murthy *et al.*, 2003).

Finally, transport of cake through high-shear conveyance systems such as cake pumps and screw conveyors could likely raise the odor production (Murthy *et al.*, 2002).

Chemical Conditioning and Dewatering of Sludge

Dewatering is one of the important drying processes since a lower volume of sludge results in cost-effective application. Chemicals are usually added to improve the efficiency of dewatering processes and the quality of the filtrate or centrate. In a municipal wastewater treatment plant, high-solids centrifuges or belt filter presses are commonly used (Novak, 2006). Dentel (2001) studied the selection of the conditioning chemicals to achieve good dewatering rates using both synthetic organic polymers and metal ions, usually iron salts. These chemicals are normally used for coagulation and removal of the colloidal fractions, aggregating them in sludge. When the optimal conditioner is used in sludge, water is separated faster (Novak, 2006).

The structure and role of floc determine the dewatering and conditioning requirements of biological sludges (Novak *et al.*, 2001). Higgins and Novak (1997a) proposed that the integral structure of floc mainly consists of biopolymer bound by cations. Poor effluent quality and dewaterability were shown to occur when monovalent cations exceed divalent cations in the wastewater influent. In addition, Higgins and Novak (1997b) showed that the most prominent constituent of floc is the protein component in the biopolymer.

Novak et al. (2003) suggested that two types of biopolymers, lectin-like proteins and a mix of proteins, polysaccharides, and humic acids exist in waste activated sludge. The lectin-like proteins are connected by Ca++ and Mg++ cation bridges to polysaccharides. Higgins and Novak (1997a) found that activated sludge settling and dewatering properties were improved, as Ca++ and Mg++ concentrations increased. In addition, the sodium content in the wastewater improved the settling and dewatering characteristics until the M/D ratio exceeded 1:1 based on an equivalent basis. When the ratio was above 2:1, sludge dewatering properties deteriorated. This problem could be overcome by addition of Ca++ and Mg++ to the feed.

A mix of proteins, polysaccharides, and humic acids in wastewater appears to be collected by aluminum and iron. The aluminum-associated fraction has been poorly studied. However, it is thought that iron content in sludge results in the release of biopolymer into solution when iron is reduced. Much of this released biopolymer consists of biocolliods with a size range between 1.5 μm and 30,000 daltons. As more floc protein is released, residual undegraded accumulates in solution. The biopolymer fraction that is released to solution and not degraded results in a higher dose of polymer and poor dewatering (Bivins and Novak, 2001). Thus, polymer dose in the sludge is determined by these colloidal

proteins that are remained and interfere with dewatering under anaerobic condition. The accumulation of the colloidal material is related to volatile solids destruction. Dewatering properties become poorer as the efficiency of anaerobic digestion increases. According to a related study by Park (2002), conditioning and dewatering properties could be predicted based on the cations content, thereby providing a tool of estimation for sludge handling costs prior to a digestion facility construction.

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Chapter 2. The Effect of Wastewater Feed Cations on Volatile Solids Destruction and Odor Control

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Abstract

The role of influent cations and addition of coagulants was evaluated for volatile solids destruction by anaerobic digestion and odor production following anaerobic digestion. Wastewater sludge samples were obtained from seven municipal wastewater treatment plants. After 30 days of anaerobic digestion in batch reactors, the chemical oxygen demand (COD) reduction, volatile solids (VS) reduction and volatile sulfur compounds (VOSCs) were measured. The data shows that aluminum addition to RAS played a role in decreasing volatile solids destruction. In addition, it lowered VOSC production. Iron addition to RAS resulted in more VS destruction and lower VOSC production. Direct addition of iron to the digesting sludge was the most efficient point of addition with respect to VS destruction and odors, increasing VS destruction and reducing headspace organic sulfur. It was also found that volatile solids destruction and VOSC production increased proportionally as iron in

influent increased. However, they decreased as the aluminum content in the influent increased.

Key Words

Anaerobic digestion, iron, aluminum, VS destruction, hydrogen sulfide, VOSCs

Introduction

Digestion is a biological process commonly used for the stabilization of sludge from wastewater treatment plants. Stabilization includes destruction of pathogens and reduction in both volatile solids (VS) and volatile organic sulfur compounds (VOSC) (Novak *et al.*, 2003). Cations, especially metals and metal-associated organic matter in the sludge, may be an important factor for prediction of the digestion performance such as solids destruction and odor generation. Basically, it is difficult to predict digestability and odor generation potential. Such prediction is of importance and cost-effective when the design of wastewater treatment is made (Novak *et al.*, 2007). In order to understand the effect of cations on anaerobic digestion, the role of cations in the floc structure of predigested sludge is of importance. Park and Novak (2007) proposed that there are iron bound organics that are degraded by anaerobic digestion, an aluminum bound fraction that is resistant to degradation under aerobic and anaerobic condition, and a divalent cation-associated fraction that can be degraded only under aerobic condition. Novak *et al.* (2003) proposed that flocs associated with iron in activated sludge are digested differently from floc material

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associated with Ca^{++} and Mg^{++}.

Recently, Park *et al.* (2006) found that volatile solids destruction of activated sludge under anaerobic conditions is dependent on the iron content in the sludge. Murthy *et al.* (2000) suggested that iron in sludge has an affinity for proteins. Iron in sludge is reduced from the +3 state to +2 when it enters the anaerobic digester and the organics associated with iron are released in combination with sulfide. Some of these released organics, but not all, are degraded in the digester, resulting in the volatile solids destruction. As iron in sludge increases, volatile solids destruction increases (Novak *et al.* 2007). In addition, VOSC from the dewatered sludge cake also increase in spite of increase in volatile solids destruction with increase in the iron content of sludge. It is thought that odors are generated by further release of protein that remained undegraded in the digester through shear, especially shear in a centrifuge. However, Novak *et al.* (2002) found that Ca^{++} and Mg^{++} associated organics are not related to odor generation from the dewatered sludge cake since Ca^{++} and Mg^{++} do not increase after centrifugation.

Anaerobically digested sludge taken directly from a digester generally has low odors. However, the dewatering process, especially centrifugation, can cause the disturbance of the balance between the production and degradation rate of VOSCs, thereby increasing odors significantly. This occurs as the result of inhibition of the sulfur consuming organisms, usually methanogens (Higgins *et al*, 2006). The factors that appear to contribute to increased odors are the dewatering equipment, polymer dose, and cake handling and transport (Higgins *et al.*, 2006). Firstly, high-solids centrifuges trigger not only more exposure to the air that leads to inhibition of methanogens that play a role in degrading

VOSCs, but also imparting more shear causing cell lysis and damage or greater floc breakup, resulting in increase in odors. Odors associated with biosolids resulted from high-solids centrifuges are usually greater than from medium-solids centrifuges which are greater than belt-filter presses (Murthy *et al.*, 2003). Secondly, an increase in polymer dose promotes isolation of soluble protein present in liquid sludge depositing the protein into the cake sludge. Thus, the increased amount of protein which is bioavailable as a substrate for the production of VOSCs could result in more odor production during storage (Higgins *et al.*, 2002, Murthy *et al.*, 2003). Lastly, transport of cake through high-shear conveyance such as cake pumps and screw conveyors could likely raise the odor production through shear of floc (Murthy *et al.*, 2002). Therefore, further study regarding the effect of feed cations and their point of addition on volatile solids destruction and odor production is necessary to better operate and design wastewater plants for managing biosolids and controlling odor problems.

Research Objectives

The objective of this study was to determine the impact of aluminum and iron on anaerobic digester performance and odorant production. Specifically addressed were:

(1) effects of anaerobic digestion without chemical addition on digestability of wastewater and generation of organic sulfur compounds (e.g. methanethiol, dimethyl sulfide, dimethyl disulfide);

(2) effects of chemical addition such as aluminum and iron for phosphorus removal to the waste activated sludge on digestability of wastewater sludge and VOSC generation; and

(3) effects of addition of iron as a feed for controlling hydrogen sulfide directly to the digester on digestability of wastewater sludge and VOSC generation.

Methods and Materials

Experimental Approach In order to control and reduce the effect of experimental variables, sludge storage and organic loading of digester were consistent for each sample (Smith, 2006). Seven different primary and secondary sludges were obtained from municipal wastewater treatment plants (WWTPs) and shipped to Virginia Tech using cool boxes. They were stored in a refrigerator immediately. Those plants are designated by letter from A to G. The primary and secondary sludge were thickened by low speed centrifuge to maintain consistent total solids. The target TS of predigested sludge was 2.5 percent.

The cation concentrations, especially aluminum and iron, in primary sludge, given Table 1, were measured before digestion. Anaerobic digestion was carried out in the laboratory adding iron and aluminum to the wastewater activated sludge for phosphorus removal practice or iron as a feed directly to anaerobic digester for hydrogen sulfide control. Plant D does not have primary sludge so cation contents were measured in the wastewater activated sludge. It is thought that plant E and F practice chemical addition in the treatment

process since plant E has high concentration of both iron and aluminum and plant F has the highest concentration of iron.

The chemical coagulant dosage of aluminum and iron used to remove phosphorus was determined based on jar test with waste activated sludge from plant A as shown in Figure 1. Three moles of each coagulant chemical per a mole of phosphorus were selected at which more than 90% of phosphorus removal was achieved. Also, iron as 1.25 % equivalent amount of dry sludge as Fe was added to anaerobic digester for hydrogen sulfide control to simulate municipal wastewater treatment plants.

Predigested sludge involved one liter of each primary and secondary sludge. It was fed to digester with a half liter of seed sludge and anaerobically digested in batch digester for 30 days at 37°C in the constant temperature room. The seed sludge was obtained from an anaerobic digester of the plants. With the data obtained before and after digestion, the effect of influent cations concentration, total solids destruction, volatile solids destruction, COD removal, gas volume production, and organic nitrogen catabolism has been assessed. In addition, organic sulfur compounds have been measured from dewatered solids cake anaerobically digested in both field and laboratory. For simulating centrifugal dewatering, chemical conditioning was performed to find optimum dose of cationic polymer before dewatering process. Thirty seconds of blending with G of approximately $10,000s^{-1}$ were followed (Muller *et al*., 2004). The cationic polymer bound samples were dewatered in a laboratory centrifuge and then the pellet was made through a laboratory press to achieve cake solids similar to a high solids centrifuge (Novak *et al*., 2007).

Volatile organic sulfur compounds were measured in the headspace of the 250mL serum bottles with Teflon[tm] coated septa on a regular basis during incubation. 100ul of headspace gas was manually injected to the gas chromatograph and quantified by comparing the experimental chromatograms to those of gas standards (Higgins *et al.*, 2006).

The concentration of hydrogen sulfide, methanethiol, dimethyl sulfide, and dimethyl disulfide was measured and total volatile organic sulfur compounds (TVOSCs) in ppmv were calculated. The relationship between hydrogen sulfide and TVOSC and storage time in the lab digested sludge from seven municipal wastewater treatment plants is illustrated in Figure 2. The peak VOSCs were shown at day 8 in plant A, day 6 in plant B, day 8 in plant C, day 6 in plant D, day 10 in plant E, day 8 in plant F, and day 6 in plant G individually as presented in Figure 2. The concentration of methanethiol was the highest on the day when peak VOSCs were observed. This is in good agreement with findings by Novak *et al.* (2006) who showed that the MT accounts for the highest portion of VOSCs concentration during storage of anaerobically digested sludge cake.

Lomans *et al.* (1999 a); Lomans (1999 b); and Lomans *et al.* (1999 c) suggested that methanogenic bateria degrade methanethiol and dimethyl disulfide to sulfide. Higgins *et al.* (2006) also proposed that hydrogen sulfide can be converted from dimethyl sulfide or dimethyl disulfide. Thus, Figure 2 shows the general pattern of the configuration of hydrogen sulfide and organic sulfur production as the incubation time increases. The hydrogen sulfide and VOSCs generated from the other conditions also followed the similar trend and their peak values were close to those of the field digested sludge.

Analytical Methods Liquid samples were analyzed for total solids (TS), volatile solids (VS), pH, soluble total Kjeldahl nitrogen (TKN), ammonium (NH_3-N), and soluble COD according to *Standard Methods* (APHA *et al*., 1995).

The concentration of iron and aluminum in influent wastewater was measured using EPA method 3050B (acid digestion for metal analysis of soils, sediments, and sludges). Metals in the samples were quantified using an AA. Metal concentrations were expressed as mg/g TS.

A liquid cationic polymer, Clarifloc 3275, high molecular weight polymer, at 1 % (w/w) was used as sludge conditioner in this study. Optimum dosages of each conditioner were determined using a capillary suction time (CST) test by reading the lowest value. CST was an indicator of the sludge dewatering rate according to the method described by Method 2710G (APHA *et al*., 1995). Waring Blender which has 1/5 H.P. was used with a 100 ml standard sample size.

Analysis of orthophosphorus ions was performed by an ion-chromatograph from DIONEX.

Gas was collected in a tedlar bag and the gas volume was measured with peristaltic pump that has been characterized as flow rate of 0.913 L/min and standard deviation of 4.84% when one liter of gas bag was used for calibration ten times.

Results and Discussion

Background of anaerobic digestion without chemical addition

A mixture of primary and secondary sludge in the ratio of 1 to1 has been anaerobically digested in the constant temperature room to see the characteristics of digestibility and odor production of lab digested sludge. Volatile solids destructions in plant A, B, C, E, and G were within 36 to 44 percent in Table 2. However, VS destruction in plant D was relatively low (26.57 percent). Plant F had the highest volatile solids removal (47.17 percent) among them. These results show that VS destruction is dependent on influent aluminum or iron content since plant D had 1.87 mg/g TS of iron and plant F had 10.50 mg/g TS of iron in influent. In other words, VS destruction increases as iron content in influent increases since iron associated organics can be released easily and degraded in anaerobic digester (Novak *et al.*, 2007). Thus, it is expected that plant E would have high VS destruction since it had high concentration of iron (9.20 mg/g TS) in influent.

In Table 2 to 5, biogas generation rates with no chemical addition were higher than that of other digester feeds except plant E and F data which have high iron or aluminum concentration. This result is consistent with the data shown from Smith and Carliell-Marquet (2008) since substrates were more available for degradation than those from iron-dosed sludge so short releasing and hydrolyzing time might affect the rate of biogas production. They also showed that more than 70 percent of the produced biogas consisted mainly of methane gas resulted from relatively more dissolved CO_2 in anaerobic digesters (Banks, 2007).

Addition of Iron and Aluminum to practice phosphorus removal

The addition of aluminum and iron to RAS was carried out for phosphorus removal before anaerobic digestion. As shown in the Table 3, as aluminum was added to RAS, the lowest percentages of volatile solids destruction were observed in all plants but plant G. The result is consistent with the findings of Dentel and Gossett (1982) that the chemical coagulation of organic materials with aluminum in the activated sludge led to decrease in volatile solids. It is also in accord with the suggestion by Park and Novak (2007) that aluminum associated organics under anaerobic condition are not readily biodegradable. Thus, aluminum addition to RAS plays a role in decrease in volatile solids destruction.

The chemical addition of iron to RAS showed higher volatile solids destruction than no chemical addition and aluminum addition to RAS from most plants as shown in Table 4. Smith and Carliell-Marquet (2008) also showed that iron-dosed RAS generated more VS destruction from less biogas production in the first survey when anaerobic digestion was tried with only RAS fed to digester. However, the extent of volatile solids removal was basically lower than that when iron was directly added to anaerobic digesters except in plant E in which iron and aluminum concentrations were unexpectedly high in influent. Iron addition to RAS might result in increasing release of iron bound organics, thereby being more degraded.

Direct Addition of Iron to digester

Similar to iron addition to RAS, iron added to a digester also increases in iron bound organics that are easily degradable. Therefore, volatile solids destruction from the

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anaerobically digested sludge with direct addition of iron to the digester was greater than other practices in most plants as shown in Table 5. Especially, the extent of VS destruction when iron was added to the digester as a feed is normally higher than when iron was added to RAS in all plants but plant E. This result shows that direct addition of iron to the anaerobic digester as a feed is the most efficient in aspect of VS destruction. Along with volatile solids destruction, large amount of gas was produced compared to aluminum and iron added to RAS.

Lomans *et al*. (1999 a); Lomans (1999 b); and Lomans *et al*. (1999 c) showed that precipitation of sulfide as FeS is caused by addition of ferric chloride to a pure culture of *Methanococcoides hollandica*. It is thought that iron is a useful coagulant for wastewater treatment in the plant where odor problems associated with hydrogen sulfide are of great concern. Iron dose played a role in notable decrease in peak organic sulfur concentration easily shown in bar charts as Figure 3. Iron addition to digester for hydrogen sulfide control resulted in VOSCs generation inhibited by removing substrate for the odor cycle. This result was similar to that of iron addition to RAS. However, its efficiency can be highly evaluated over the point of addition of iron or aluminum to RAS. Therefore, direct iron addition to anaerobic digester has advantages in enhanced VS destruction and lowering odor production regardless of influent cations concentration.

VS destruction and VOSCs as variation of feed cations in influent

It is indicated that influent iron or aluminum content has a strong correlation with both volatile solids destruction after anaerobic digestion and organic sulfur gas production from

centrifugally dewatered sludge cake as shown in Figure 4 to 7. The relationship between the cations in influent and volatile solids destruction was almost logarithmic so that as the amount of iron content in influent increased, volatile solids destruction also increased. In addition, an increase in aluminum in the influent led to a decrease in volatile destruction as illustrated in Figure 4 and 5. These results are consistent with the previous data from Park *et al*. (2006). The upper dashed lines in figure 4 and 5 indicate VS destruction of iron addition to digesters. Basically, iron bound organics are readily biodegraded as iron increases in the influent. Therefore, further addition of iron preferably to digesters resulted in greater volatile solids destruction. Conversely, aluminum bound organics are as easily degraded when more aluminum is present in influent. When aluminum was added to RAS for phosphorus removal, VS destruction was slightly lowered.

As shown in Figures 6 and 7, VOSCs generation was proportionally related to influent iron, but inversely related to influent aluminum when no chemicals were added after anaerobic digestion. VOSCs concentrations when aluminum or iron was added to RAS or digesters were lower than those values and scattered under the solid line. They were not drawn in Figures 6 and 7. It is thought that aluminum addition to RAS inhibited the role of iron to have iron bound organics degraded to cysteine and methionine and iron addition to RAS or digesters reduced the hydrogen sulfide concentration to prevent H_2S from being methylated to MT and DMS. Thus, these plotted graphs support the idea that iron and aluminum behave in the opposite way during anaerobic digestion processes.

Conclusions

This study based on the data collected under anaerobic condition has shown that volatile solids destruction and VOSCs had strong correlation with aluminum and iron in wastewater influent and their point of addition. The specific conclusions are as follows:

• Aluminum addition to RAS resulted in decrease in VS destruction due to aluminum bound organics that are not easily biodegradable. In addition, VOSCs production was less than sludge with no chemical addition due to inhibition of VOSCs generation.

• Iron addition to RAS showed more VS destruction than no chemical addition or aluminum addition to RAS. The hydrogen sulfide was controlled by adding iron to RAS, thereby reducing VOSCs production since precursors for VOSCs were removed. This result is more efficient than that of aluminum addition to RAS.

• Direct addition of iron to digester led to increase the most in VS destruction and significant decrease in VOSCs production. It is thought that the addition of iron as feed to digester could be the most efficient point of addition increasing VS destruction and reducing headspace organic sulfur.

• VS destruction increased proportionally as concentration of iron in influent increased since iron bound organics are readily biodegradable. However, VS destruction decreased as aluminum content in influent increased in that aluminum bound organics are not much degraded in digester. When addition of iron preferably to anaerobic digester was carried

out, higher VS destruction was achieved. In contrast, as aluminum is added to RAS for phosphorus removal, lower VS destruction was observed in both cases.

• VOSCs production also increased when influent iron in sludge increased. However, it decreased as influent aluminum content increased in sludge when no chemicals were added under anaerobic condition. When aluminum or iron was added to sludge, VOSCs production was lower than the above.

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Table 2.1 − Total aluminum and iron content in influent from seven municipal WWTPs.

WWTP	Cations in influent (mg/g TS)	
	Fe	Al
A	3.90	2.48
B	3.83	2.44
C	5.09	0.51
D	1.87	3.76
E	9.20	15.95
F	10.50	0.94
G	3.77	2.41

Table 2.2 − Characteristics of lab digested sludge from seven municipal WWTPs without adding chemicals.
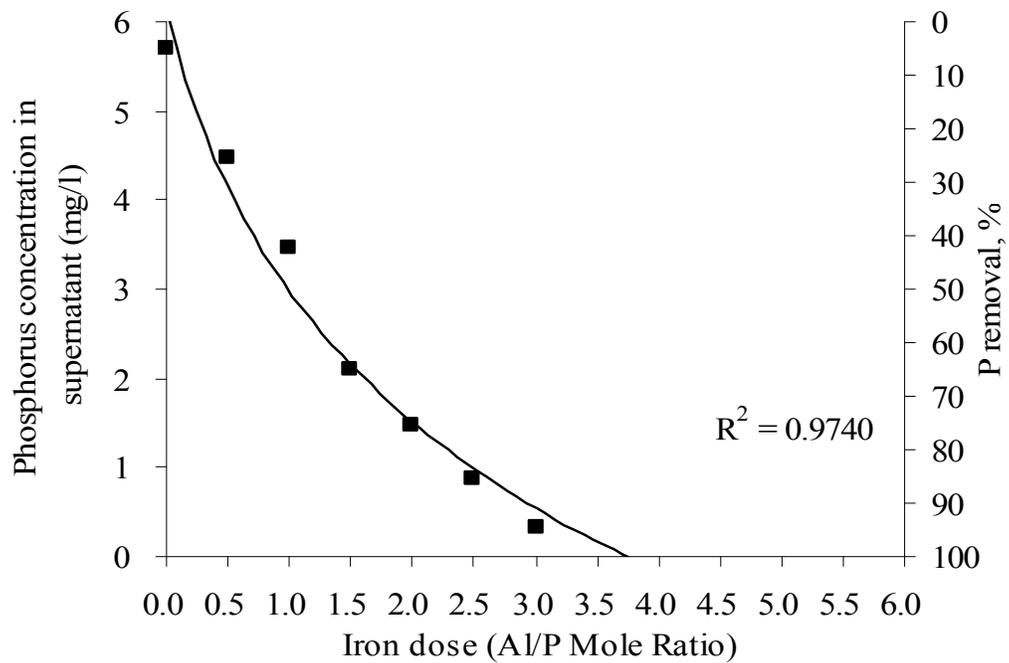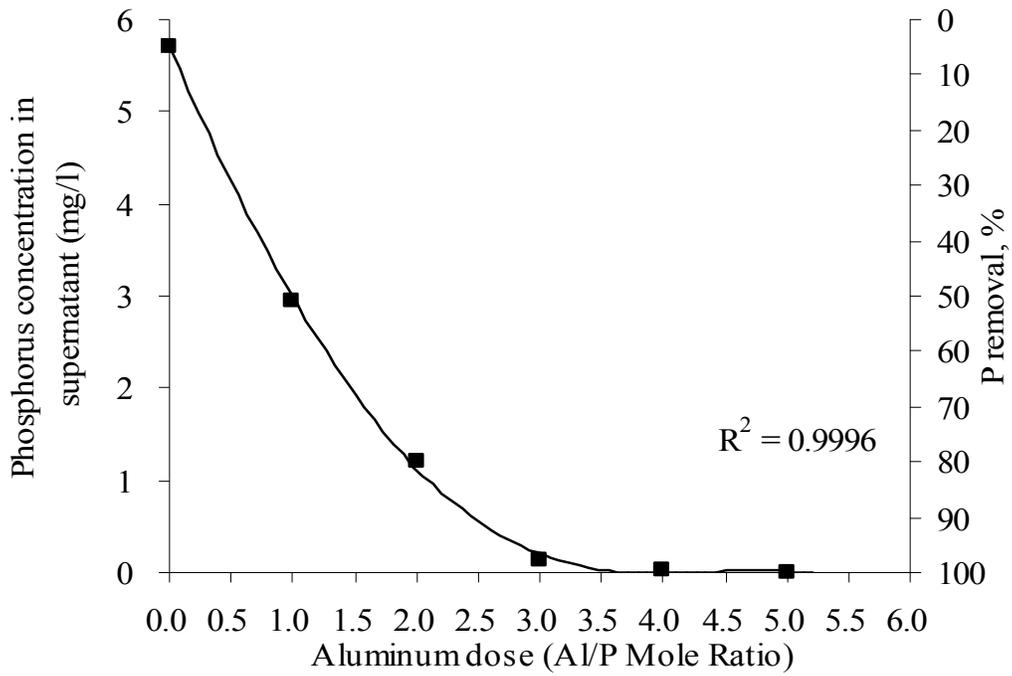
WWTP	TS removal (%)	VS removal (%)	COD removal (%)	Biogas production (ml / % VS removal)	Organic N removal (%)	Optimum polymer dose (g/kg TS)	CST (s)
A	30.41	39.44	51.95	333.77	26.11	3.38	8.45
B	29.68	36.65	45.38	398.08	12.57	3.84	27.10
C	27.14	42.54	62.67	454.25	44.25	3.78	11.00
D	19.92	26.57	67.95	605.36	32.05	2.63	19.40
E	32.53	43.92	65.32	609.02	41.17	4.03	22.40
F	39.41	47.17	35.88	236.78	42.43	3.82	65.40
G	31.23	37.77	49.77	381.55	50.43	3.99	14.70

Table 2.3 − Characteristics of lab digested sludge from seven municipal WWTPs after adding aluminum to RAS for phosphorus removal.

WWTP	TS removal (%)	VS removal (%)	COD removal (%)	Biogas production (ml / % VS removal)	Organic N removal (%)	Optimum polymer dose (g/kg TS)	CST (s)
A	30.87	38.82	50.10	335.83	21.39	2.91	8.85
B	26.49	33.97	28.57	366.48	25.02	4.12	40.40
C	33.65	41.34	53.33	375.80	46.05	4.73	13.80
D	16.82	24.21	67.61	348.21	33.64	1.99	15.80
E	35.76	43.76	61.50	248.95	46.50	4.01	64.00
F	37.13	43.91	6.75	88.71	28.83	3.90	35.70
G	28.02	34.14	14.1	295.02	47.53	3.63	14.30

Table 2.4 − Characteristics of lab digested sludge from seven municipal WWTPs after adding iron to RAS for phosphorus removal.

WWTP	TS removal (%)	VS removal (%)	COD removal (%)	Biogas production (ml / % VS removal)	Organic N removal (%)	Optimum polymer dose (g/kg TS)	CST (s)
A	30.34	41.24	49.91	297.32	21.10	3.00	8.55
B	25.35	38.72	19.40	354.34	9.83	2.72	39.60
C	33.72	43.33	50.22	367.36	35.71	4.42	31.85
D	16.85	28.47	66.60	133.08	30.01	2.09	20.80
E	37.13	46.42	72.18	705.06	57.69	4.63	22.30
F	36.16	44.67	7.94	440.79	39.38	3.90	33.10
G	25.63	32.94	18.21	217.57	44.26	3.41	34.70

Table 2.5 − Characteristics of lab digested sludge from seven municipal WWTPs after adding feed iron to anaerobic digester for hydrogen sulfide control.

| WWTP	TS removal (%)	VS removal (%)	COD removal (%)	Biogas production (ml / % VS removal)	Organic N removal (%)	Optimum polymer dose (g/kg TS)	CST (s)
A	25.94	42.57	42.83	330.60	18.20	2.55	10.10
B	26.80	41.46	14.84	383.61	20.66	2.72	35.60
C	17.16	43.62	44.00	386.55	37.57	2.77	38.90
D	22.59	32.70	63.72	555.18	52.81	2.73	14.10
E	35.11	44.26	66.60	643.65	50.60	3.64	29.50
F	34.44	44.70	34.65	449.71	44.18	3.56	61.50
G	25.83	34.63	38.74	265.39	48.86	2.11	55.50

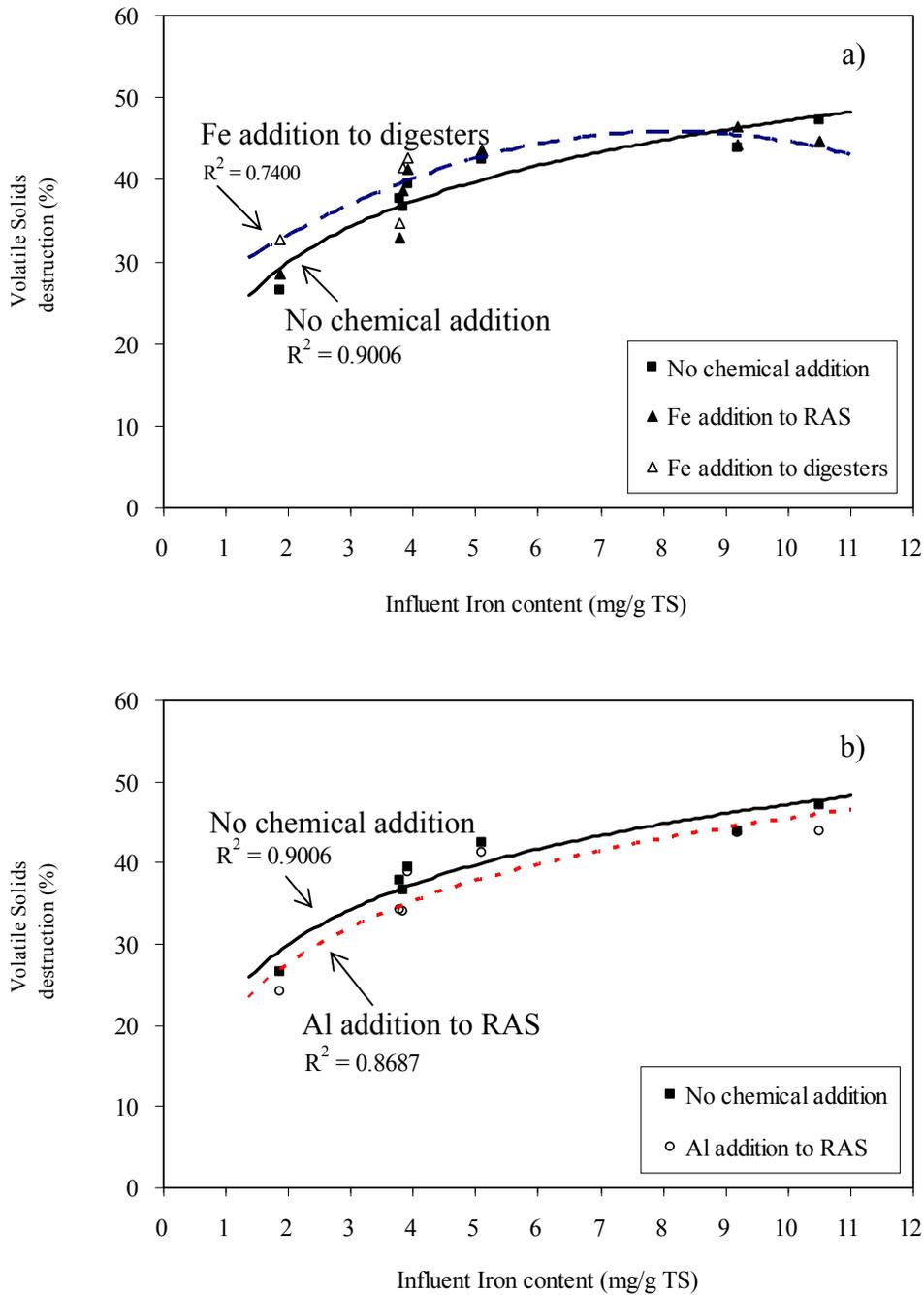**Figure 2.1** − Jar test results for selecting the optimum dose of Aluminum and Iron for phosphorus removal in WAS.
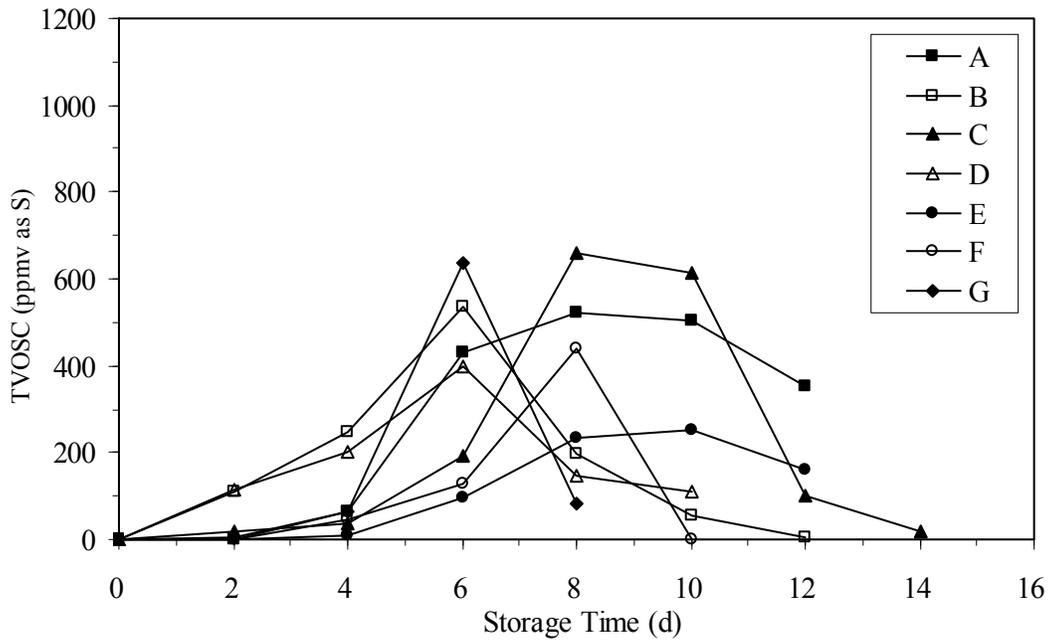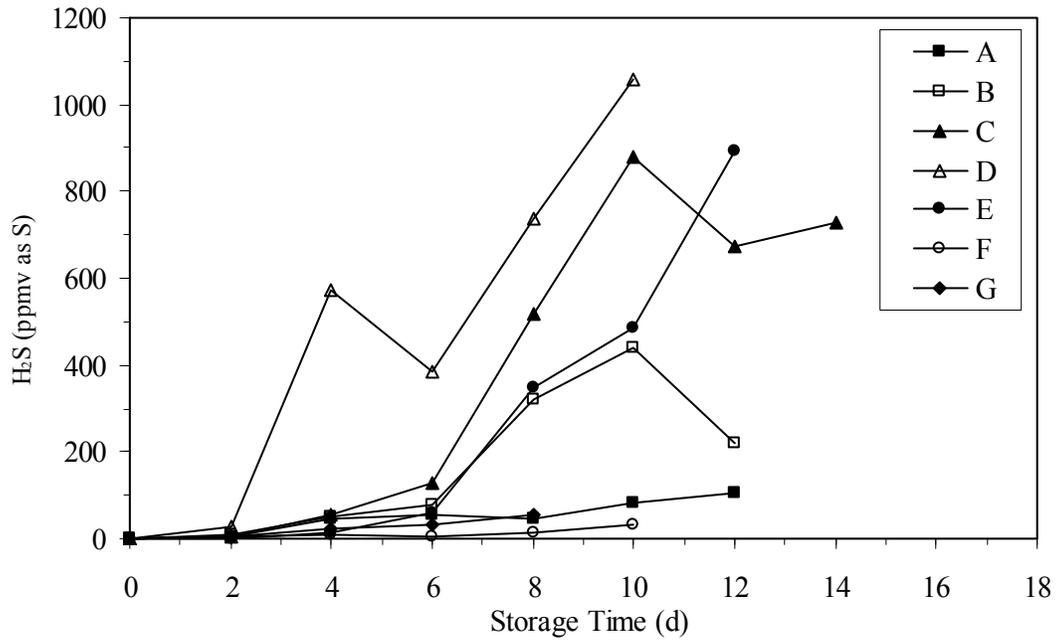
Figure 2.2 − H2S and VOSCs concentrations of lab digested sludge from seven municipal WWTPs without adding chemicals.
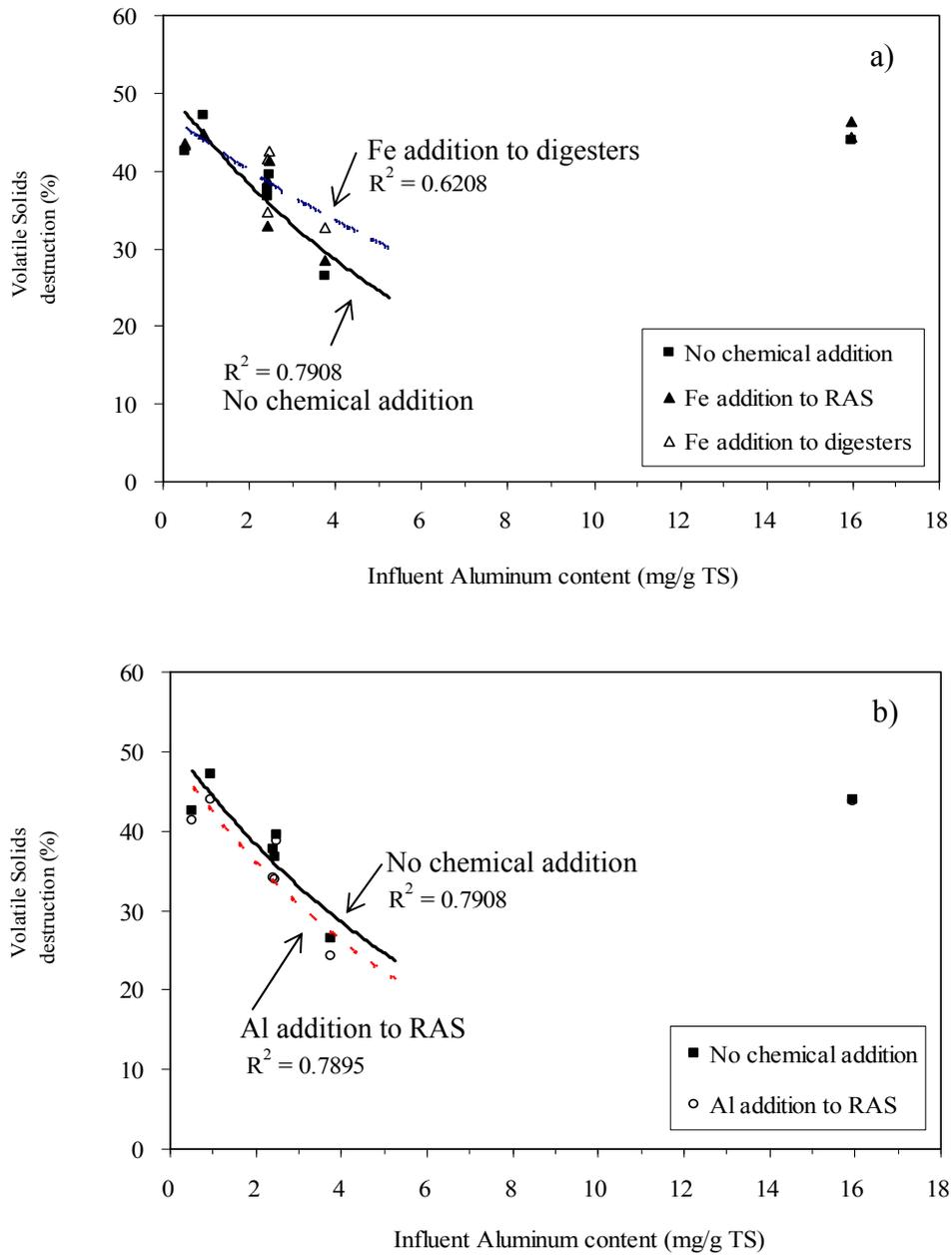
Figure 2.3 − Comparison of peak VOSCs of different anaerobic digesters from seven municipal WWTPs.

Plant E

Plant F

Plant G
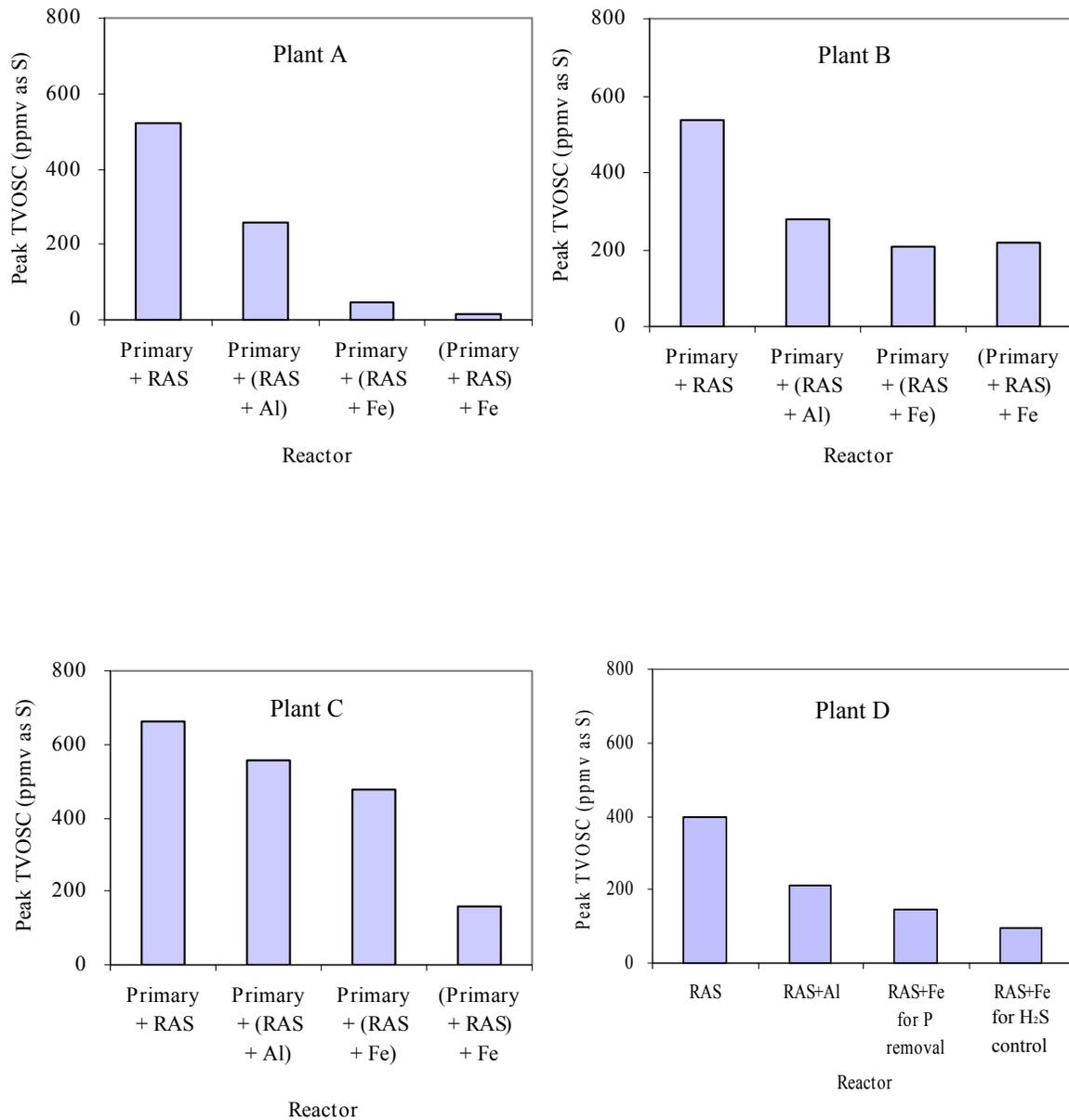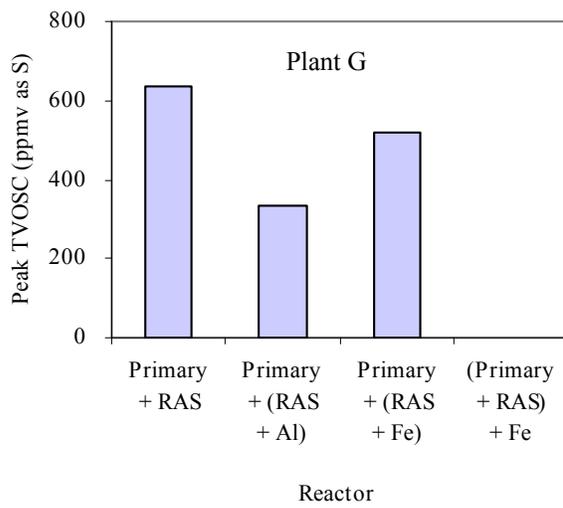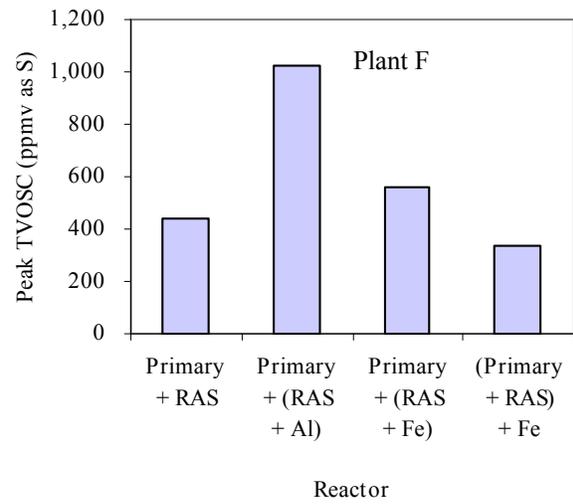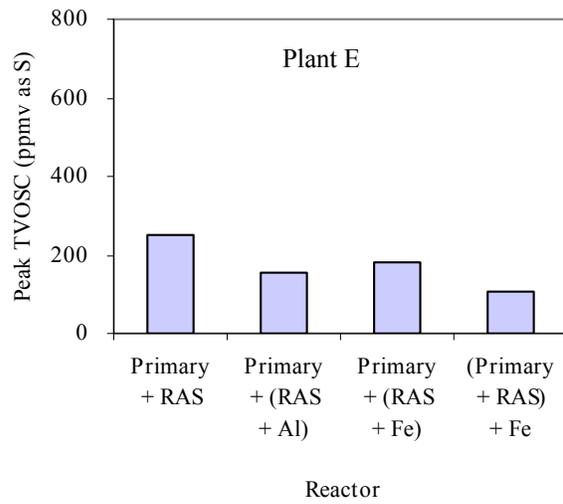
Figure 2.4 − Iron content in influent versus Volatile Solids destruction when (a) no chemical and Iron were added to sludge and (b) no chemical and Aluminum were added to RAS.

Figure 2.5 − Aluminum content in influent versus Volatile Solids destruction when (a) no chemical and Iron were added to sludge and (b) no chemical and Aluminum were added to RAS. The regression lines were obtained without the highest aluminum content data.
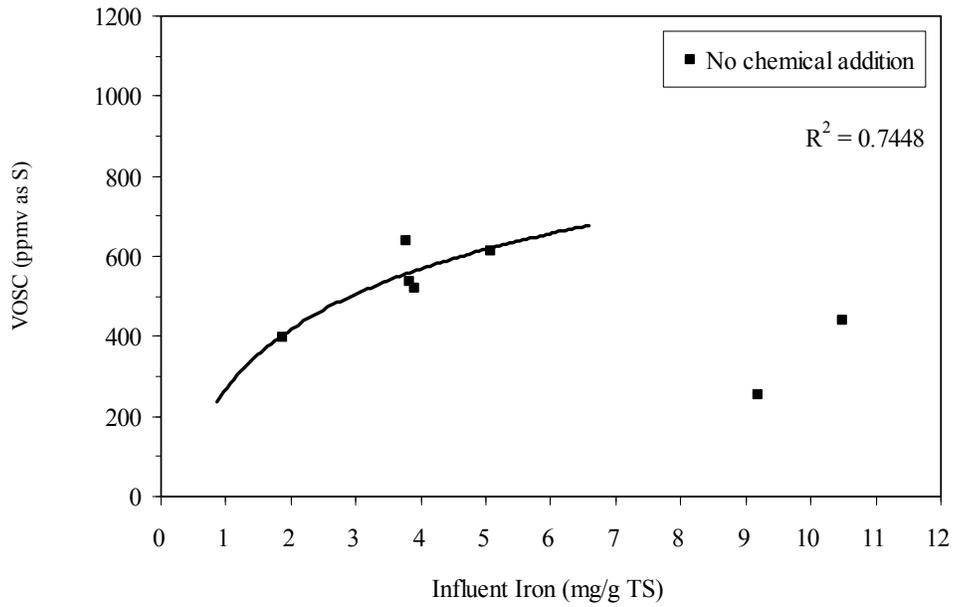
Figure 2.6 − Iron content in influent versus VOSC concentrations of dewatered sludge cake when no chemical was added to sludge. The regression line was drawn without the two highest iron content data.
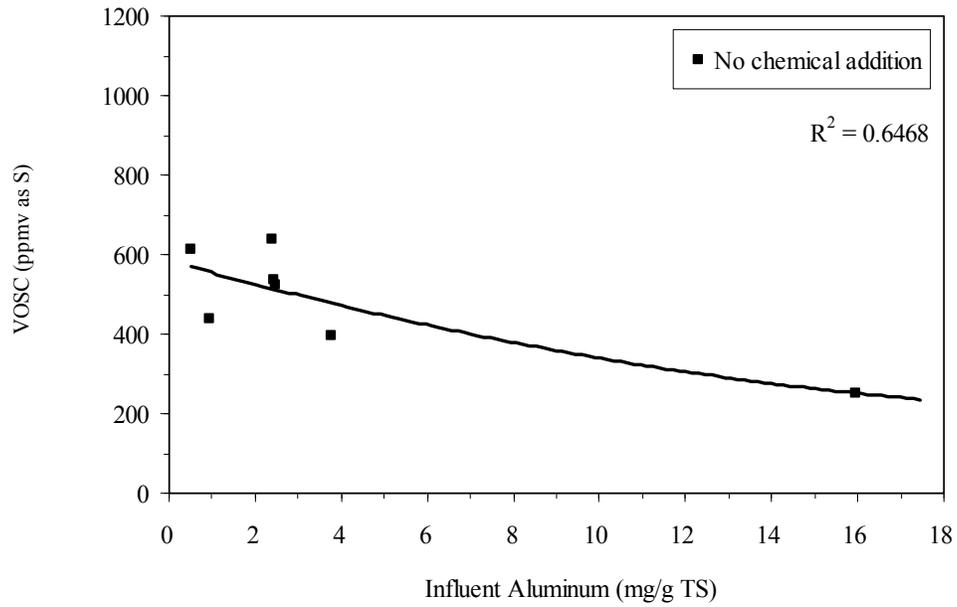
Figure 2.7 − Aluminum content in influent versus VOSC concentrations of dewatered sludge cake when no chemical was added to sludge.

Chapter 3. Relationship between Cations and Dewatering Characteristic of Biosolids following Anaerobic Digestion

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Relationship between Cations and Dewatering of Biosolids during Anaerobic Digestion

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Abstract

The dewatering characteristics of anaerobically digested sludges were analyzed for sludges generated when iron or aluminum was applied to wasted activated sludge (WAS) or when iron was added to the digester feed. Batch anaerobic digestion of the sludges was performed in the laboratory for 30 days. Conditioning with cationic polymer and dewatering simulating a high solids centrifuge were carried out following digestion. Data collected from this study shows a strong correlation between influent cations and optimum polymer conditioning dose for anaerobically digested sludge. As the iron content in the raw sludge increased, a higher optimum polymer dose was needed for dewatering. In contrast, an increase in the aluminum content in the influent resulted in a decrease in the amount of polymer required. When iron or aluminum were added to sludge before digestion, the optimum polymer dose was lowered. In addition, it is found that the direct addition of iron to digester feed was the most effective with regard to reducing the optimum polymer dose.

Key Words

Anaerobic digestion, iron, aluminum, dewatering, conditioning, CST, optimum polymer

Introduction

Dewatering is one of the most important processes for sludge handling and disposal since a lower volume of sludge results in lower costs. Chemicals are usually added to improve the efficiency of dewatering processes and the quality of the filtrate or centrate. In a municipal wastewater treatment plant, high-solids centrifuges or belt filter presses are commonly used for dewatering (Novak, 2006). Dentel (2001) studied the selection of conditioning chemicals to achieve good dewatering rates using both synthetic organic polymers and metal ions, usually iron salts. These chemicals are normally used for coagulation and removal of colloidal particles, aggregating them in the sludge. When the optimal conditioner type and dose is used in sludge dewatering, water is separated faster (Novak, 2006).

The structure and role of floc determine the dewatering and conditioning requirements of biological sludges (Novak *et al.*, 2001). Higgins and Novak (1997a) proposed that the internal structure of floc consists primarily of biopolymer bound by cations. Poor effluent quality and dewaterability were shown to occur when monovalent cations exceed divalent cations in the wastewater influent. In addition, Higgins and Novak (1997b) showed that the most prominent constituent of floc is the protein component of the biopolymer. A mix of proteins, polysaccharides, and humic acids in wastewater appears to be collected by

aluminum and iron. The aluminum-associated fraction has been poorly studied. However, it is thought that iron in sludge can be reduced during anaerobic digestion, releasing biopolymer into solution. Much of this released biopolymer consists of biocolliods with a size range between 1.5 μm and 30,000 daltons. As more floc protein is released, residual undegraded biopolymer accumulates in solution. The biopolymer fraction that is released to solution and not degraded results in a higher requirement for conditioning polymer and poor dewatering (Bivins and Novak, 2001). Thus, the optimal polymer dose in the sludge is determined by the colloidal proteins that remain undegraded and interfere with dewatering. The accumulation of colloidal material in solution is related to volatile solids destruction. As more solids are degraded, more colloids accumulate in solution. Thus, dewatering properties become poorer as the efficiency of anaerobic digestion increases. According to a related study by Park (2002), conditioning and dewatering properties could be estimated based on the cation content of the raw wastewater, thereby providing a tool for estimation for sludge handling costs prior to construction of a digestion facility.

Methods and Materials

Experimental Approach In order to reduce the effect of experimental variables, sludge digestion time and organic loading of the digester were kept consistent for each sample (Smith, 2006). Both primary and secondary sludges were obtained from seven municipal wastewater treatment plants (WWTPs) and shipped to Virginia Tech on ice. They were refrigerated immediately. Those plants are designated by letters from A to G.

The primary and secondary sludge samples were thickened by low speed centrifuge to a target total solids of 2.5 percent. Cations in the raw sludge were analyzed and conditioning and dewatering studies were conducted for anaerobically digested sludges. It was found that plants E and F had high concentration of iron and plant E had high concentration of aluminum.

Iron and aluminum were added to waste activated sludge (WAS) for phosphorus removal. In addition, for another set of samples, iron was fed directly to sludge prior to anaerobic digestion. Iron is frequently added to anaerobic digesters for hydrogen sulfide control. The chemical dosage of aluminum and iron for phosphorus removal was determined by jar testing as shown for WAS from plant A in Figure 1. Three moles of aluminum or iron per mole of phosphorus was ultimately selected as the iron and aluminum dose for all sludges. This dose can reduce phosphorus to concentrations below 0.5 mg/L. In addition, iron salt as 1.25 % of dry sludge as Fe was added directly to sludge prior to anaerobic digestion.

One liter of primary and one liter of secondary sludge were placed in four-liter batch anaerobic digesters and seeded with sludge from an anaerobic digester. The ratio of predigested sludge to seed sludge in the reactor was 4 to 1 by volume. Digestion was conducted for 30 days at 37°C in a constant temperature room. Continuous mixing was provided by magnetic stirrers. A rubber stopper, pierced with a glass tube served as a gas collector, was placed on digester and sealed tightly to avoid gas leakage. Gas was collected in a tedlar bag.

In order to simulate centrifugal dewatering, chemical conditioning was carried out to determine the optimum dose of cationic polymer for centrifugal dewatering. Thirty seconds of blending was used to simulate the shear in a centrifuge with G of approximately 10,000s^{-1} (Muller *et al*., 2004). Samples conditioned with cationic polymer were dewatered in a laboratory centrifuge and then the pellet was concentrated through a laboratory press to obtain cake solids similar to a high solids centrifuge (Novak *et al*., 2007).

Analytical Methods Iron and aluminum contents in the raw sludge were measured using EPA method 3050B (acid digestion for metal analysis of soils, sediments, and sludges). Metals in the samples were quantified using flame atomic absorption method. Metal concentrations were expressed as mg/g TS.

Total solids (TS) and total volatile solids (VS) were measured according to Standard Methods (APHA, 1995). Volatile solids destruction was determined by the formula of (VS $_{initial}$ - VS $_{final}$) / VS $_{initial}$.

A liquid cationic polymer, Clarifloc 3275, high molecular weight polymer, at 1 % (w/w) was used as sludge conditioner in this study. Optimum dosages for each conditioner were determined using a capillary suction time (CST) test by measuring the polymer dose with the lowest CST value. CST was an indicator of the sludge dewatering rate according to the method described by Method 2710G (APHA *et al*., 1995).

Analysis of orthophosphorus ions was performed by an ion-chromatograph from DIONEX.

A Waring Blender which has 1/5 HP was used to provide shear with a 100 ml standard sample size.

Results and Discussion

Data were obtained from seven anaerobically digested sludges that were digested with different metal additions as shown in table 1 to 4. These data show the characteristics of lab digested sludge with and without chemical addition to RAS or iron added prior to anaerobic digestion. Total solids (TS) percent removal, volatile solids (VS) destruction, optimum polymer dose for dewatering, total solids of dewatered solids cake, capillary suction time (CST), and influent iron and aluminum concentration were measured before and after anaerobic digestion. TS and VS results are presented in Park and Novak (2008).

For dewatering, the CST is used to analyze the rate of dewatering of digested sludge in the laboratory. In this study, the extent of dewatering was quantified by the percent dry solids of the dewatered sludge cake. However, no correlation between the influent cations and dewatered cake solids was found for the data shown in Table 4. The optimum polymer dose was obtained by dewatering the lowest value of CST in the digested sludge over a range of polymer doses (Baskerville and Gale, 1968).

The optimum dose of cationic polymer and total solids of digested sludge cake comparing four different metal addition conditions is shown in Figure 2. Except for plant D, the optimum cationic polymer dose when iron was added to anaerobic digesters was the lowest among four digestion feeds. It appears that when iron is added to a digester, it binds

to some of the organics that are released during anaerobic digestion. Novak *et al*. (2007) showed that as the iron content in sludge increased, volatile solids destruction increased. However, additional biocolloids were also released which hinders sludge from dewatering. However, addition of iron to anaerobic digesters appears to coagulate those biocolloids during digestion resulting in a reduced demand for conditioning chemicals. In addition, except for plant C and E, the highest TS in the dewatered sludge cake occurred when iron was added to digester feed. Before anaerobic digestion, it was found that plant E had high concentration of both iron and aluminum and plant F had high concentration of iron in wastewater influent. Less decrease in optimum polymer dose of plant E and F might result from high concentration of iron or aluminum affecting reduced cake solids in plant E.

The relationship between the influent iron concentration and optimum polymer dose when no additional iron or aluminum was added is shown in Figure 3. The data followed the observation by Bivins and Novak (2001) that as iron increases in sludge, a higher polymer dose is required. In this graph, linear regression lines with a high r^2 were found when aluminum or iron was added to RAS and iron was added to digester feed. Although these lines have different slopes, it is apparent that addition of iron or aluminum to sludge influences the amount of polymer needed for dewatering. When aluminum was added to RAS, the required optimum dose of polymer sharply increased. However, when iron was added to the digester feed, the optimum polymer dose was lower than that from anaerobically digested sludge with no chemical addition. As shown in Figure 3, the addition of iron to the digester was the most efficient point of addition with regard to the cationic polymer dose.

The relationship between optimum dose of polymer and the influent aluminum content is illustrated in Figure 4. It showed completely contrary result from iron in that as the aluminum content in influent increased, the optimum polymer dose decreased. However, data for plant E which had unexpectedly high aluminum content did not follow this trend. The aluminum was added in the form of alum sludge so it did not interact with organics in sludge in the same way as a dissolved iron would react. Park and Novak (2007) showed that aluminum associated organics under anaerobic condition are not readily biodegradable. Thus, lower volatile solids destruction resulted in a decrease in accumulation of the undegraded biocolloids in solution so that less polymer was needed to aggregate them for dewatering. When aluminum was added to RAS, a steeper slope was found in Figure 4. For some sludges which have low influent aluminum, the optimum polymer dose was higher than that of no chemical addition and for others which have high influent aluminum, the optimum dose was lowered than that of no chemical addition. Iron addition to RAS lowered the optimum polymer dose in digested sludge as shown in Figure 4. In addition, when iron was added to anaerobic digesters, the amount of optimum polymer dose was lowered than that of no chemical addition. However, the addition of iron to digester feed did not show any trends in Figure 4. Overall, it appears that iron addition to sludge, wherever the point of addition, resulted in decreased optimum polymer dose.

Conclusions

Data obtained before and after anaerobic digestion showed that the optimum polymer doses were strongly correlated with influent cations content, addition point of chemical coagulants, and the choice of chemicals. The following conclusions are observed:

• As iron in influent increased, the optimum polymer dose also increased since more undegraded biocolloids accumulates in solution. When aluminum was added to RAS, the required optimum polymer dose sharply increased. The values were lowered when iron was added to sludge. The addition of iron to digester feed required the lowest amount of optimum polymer dose since it played a role in coagulation of those biocolloids.

• Increase in aluminum content in influent resulted in decrease in optimum polymer dose. When aluminum was added to sludge before anaerobic digestion, a steeper decrease of the optimum polymer dose was found. However, iron addition to sludge resulted in lower optimum polymer dose to digested sludge.

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Table 3.1 − Characteristics of lab digested sludge from seven municipal wastewater treatment plants without adding chemicals.

WWTPs	TS removal (%)	VS removal (%)	Optimum polymer dose (g-polymer / kg-TS)	Dewatered cake solids (%)	CST (s)	Influent Fe (mg/g TS)	Influent Al (mg /g TS)
A	30.41	39.44	3.38	21.80	8.45	3.90	2.48
B	29.68	36.65	3.84	17.66	27.10	3.83	2.44
C	27.14	42.54	3.78	20.09	11.00	5.09	0.51
D	19.92	26.57	2.63	22.43	19.40	1.87	3.76
E	32.53	43.92	4.03	24.43	22.40	9.20	15.95
F	39.41	47.17	3.82	21.53	65.40	10.50	0.94
G	31.23	37.77	3.99	20.46	14.70	3.77	2.41

Table 3.2 − Characteristics of lab digested sludge from seven municipal wastewater treatment plants with aluminum added to RAS.

WWTPs	TS removal (%)	VS removal (%)	Optimum polymer dose (g-polymer / kg-TS)	Dewatered cake solids (%)	CST (s)	Influent Fe (mg/g TS)	Influent Al (mg /g TS)
A	30.87	38.82	2.91	23.79	8.85	3.90	2.48
B	26.49	33.97	4.12	17.66	40.40	3.83	2.44
C	33.65	41.34	4.73	20.09	13.80	5.09	0.51
D	16.82	24.21	1.99	22.43	15.80	1.87	3.76
E	35.76	43.76	4.01	24.43	64.00	9.20	15.95
F	37.13	43.91	3.90	22.27	35.70	10.50	0.94
G	28.02	34.14	3.63	20.91	14.30	3.77	2.41

Table 3.3 − Characteristics of lab digested sludge from seven municipal wastewater treatment plants with iron added to RAS.

WWTPs	TS removal (%)	VS removal (%)	Optimum polymer dose (g-polymer / kg-TS)	Dewatered cake solids (%)	CST (s)	Influent Fe (mg/g TS)	Influent Al (mg /g TS)
A	30.34	41.24	3.00	22.60	8.55	3.90	2.48
B	25.35	38.72	2.72	16.46	39.60	3.83	2.44
C	33.72	43.33	4.42	16.44	31.85	5.09	0.51
D	16.85	28.47	2.09	23.33	20.80	1.87	3.76
E	37.13	46.42	4.63	22.69	22.30	9.20	15.95
F	36.16	44.67	3.90	20.80	33.10	10.50	0.94
G	25.63	32.94	3.41	21.93	34.70	3.77	2.41

Table 3.4 − Characteristics of lab digested sludge from seven municipal wastewater treatment plants with iron added to anaerobic digester.

WWTPs	TS removal (%)	VS removal (%)	Optimum polymer dose (g-polymer / kg-TS)	Dewatered cake solids (%)	CST (s)	Influent Fe (mg/g TS)	Influent Al (mg /g TS)
A	25.94	42.57	2.55	24.77	10.10	3.90	2.48
B	26.80	41.46	2.72	22.53	35.60	3.83	2.44
C	17.16	43.62	2.77	18.02	38.90	5.09	0.51
D	22.59	32.70	2.73	25.43	14.10	1.87	3.76
E	35.11	44.26	3.64	23.41	29.50	9.20	15.95
F	34.44	44.70	3.56	23.29	61.50	10.50	0.94
G	25.83	34.63	2.11	22.51	55.50	3.77	2.41
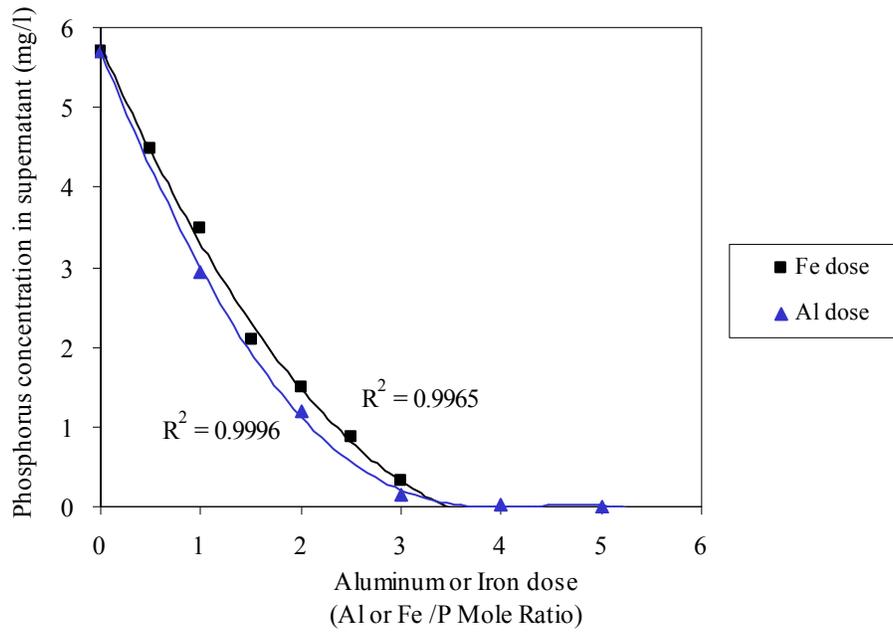
Figure 3.1 − Jar test results to select the optimum dose of Aluminum and Iron for phosphorus removal in WAS.
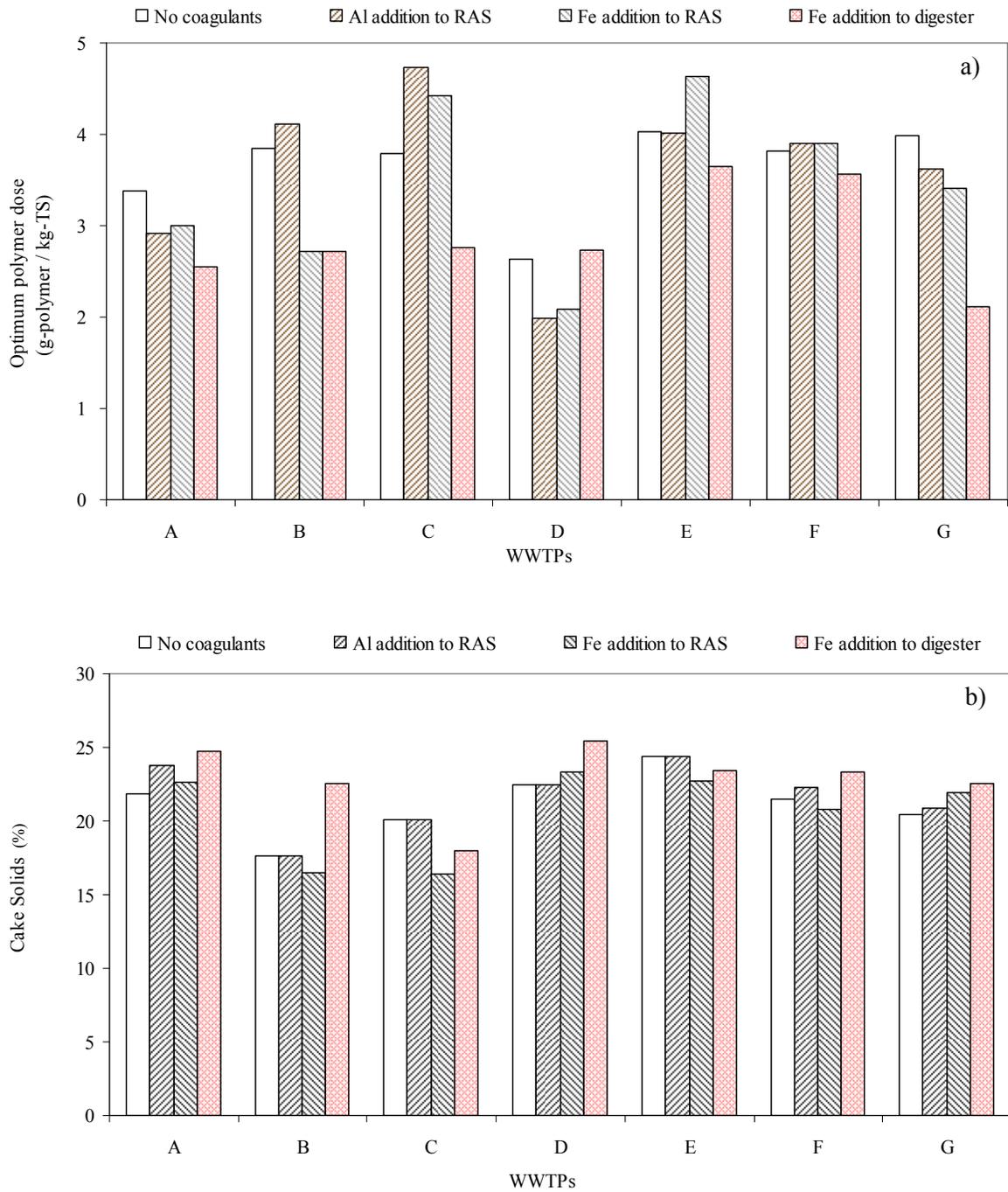
Figure 3.2 − Bar charts for (a) optimum dose of cationic polymer and (b) cake solids comparing four digestion feeds from seven municipal WWTPs.
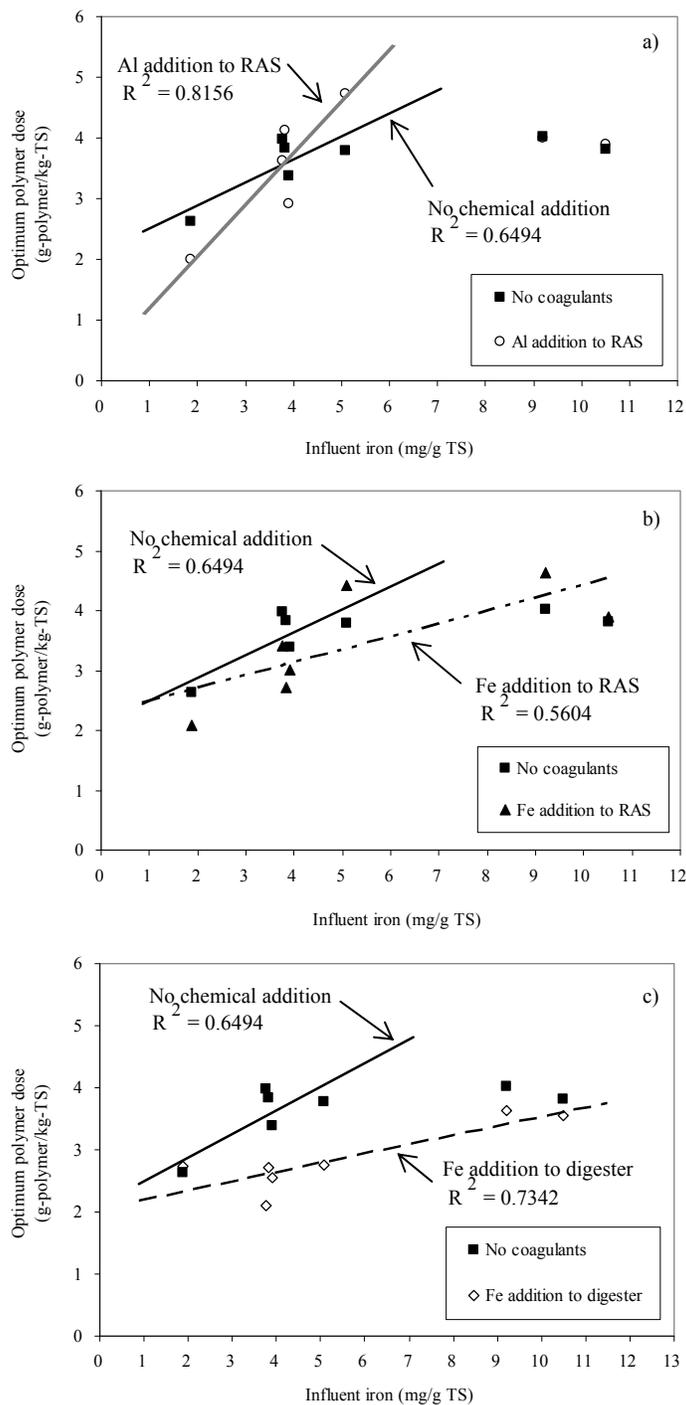
Figure 3.3 − Relationship between iron content in influent and optimum dose of cationic polymer when (a) no chemical and aluminum were added to RAS and (b) no chemical and iron were added to RAS and (c) no chemical and iron were added to digester. The regression lines are obtained without using the two highest iron content data.
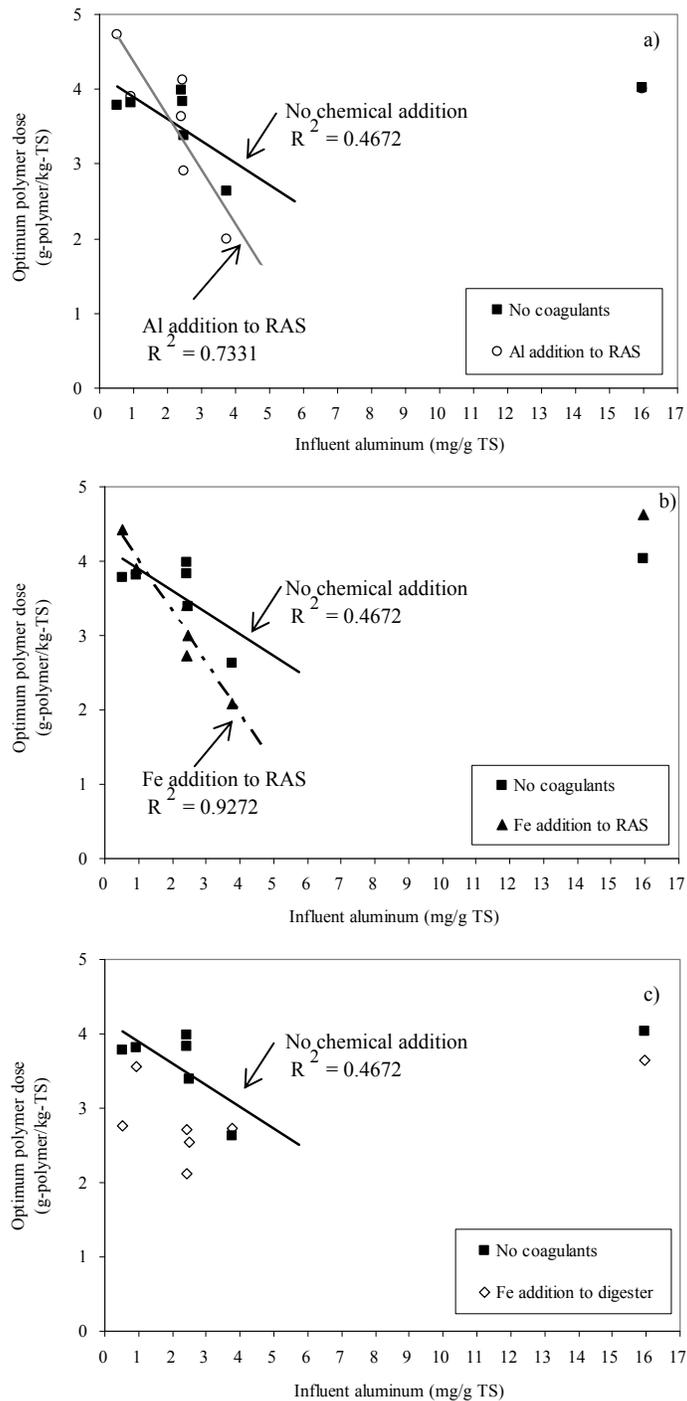
Figure 3.4 − Relationship between iron content in influent and optimum dose of cationic polymer when (a) no chemical and aluminum were added to RAS and (b) no chemical and iron were added to RAS and (c) no chemical and iron were added to digester. The regression lines are obtained without using the highest aluminum content data.
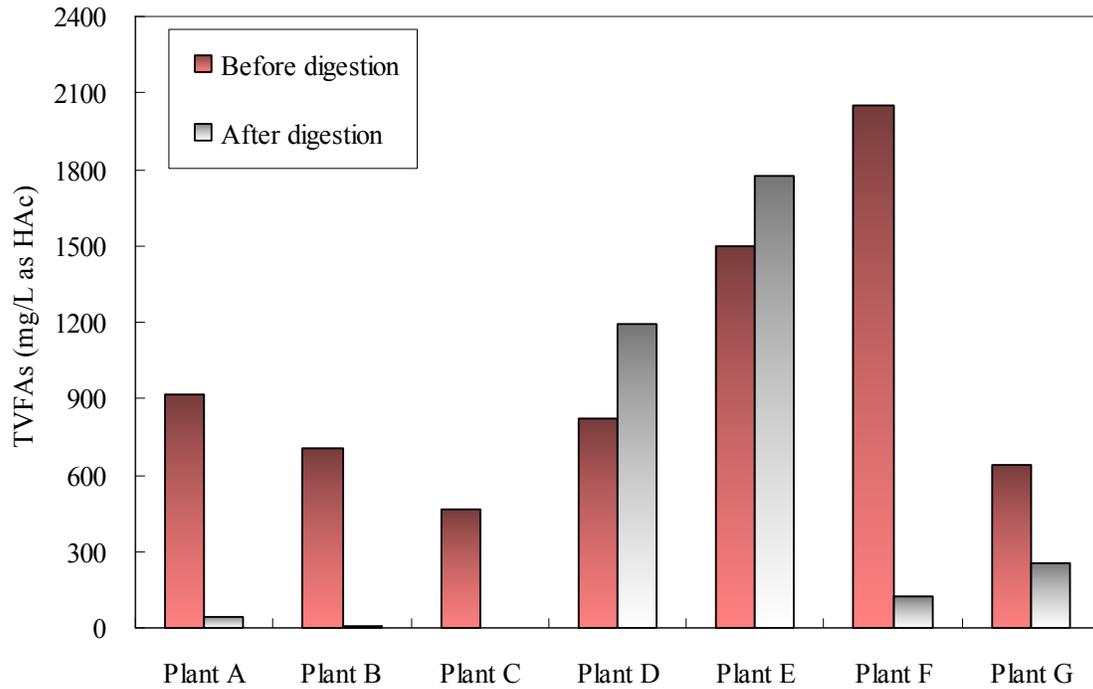
Figure A.1 − Total Volatile Fatty Acids as acetic acid before and after digestion without adding coagulants from seven municipal WWTPs.
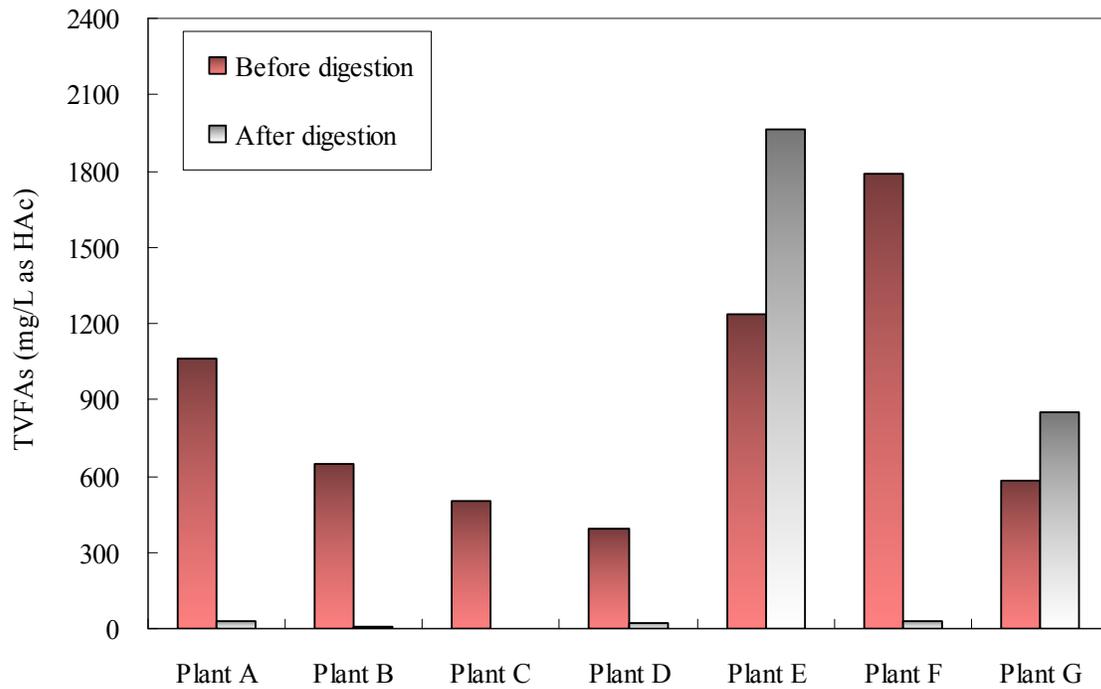
Figure A.2 − Total Volatile Fatty Acids as acetic acid before and after digestion adding Aluminum to RAS for phosphorus removal from seven municipal WWTPs.
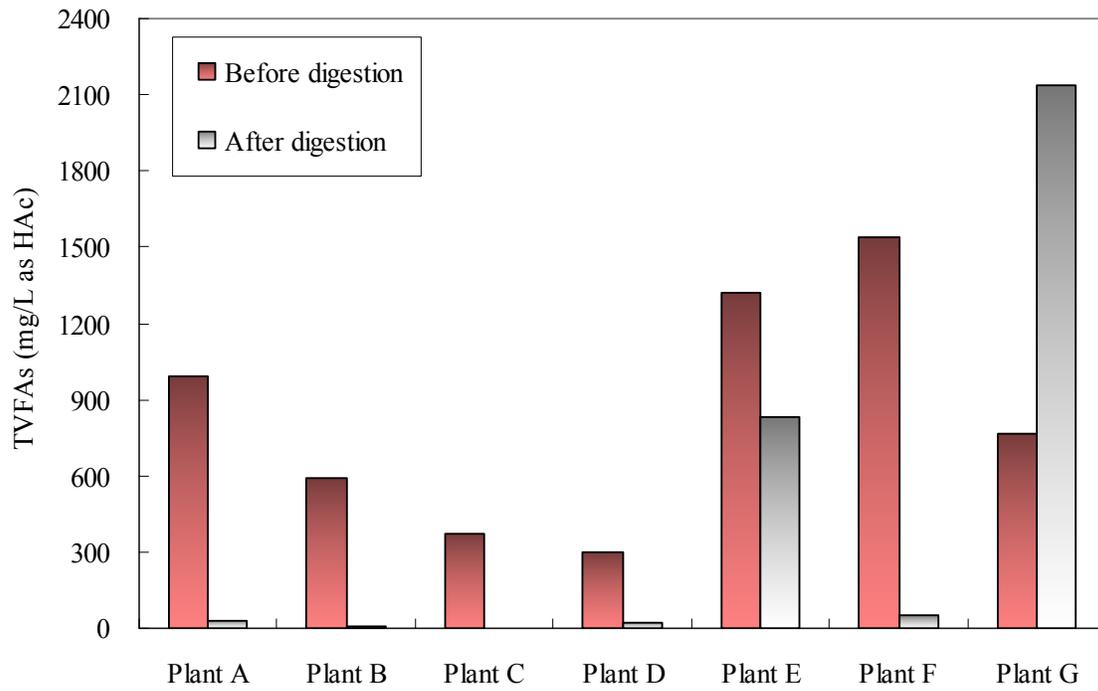
Figure A.3 − Total Volatile Fatty Acids as acetic acid before and after digestion adding Iron to RAS for phosphorus removal from seven municipal WWTPs.
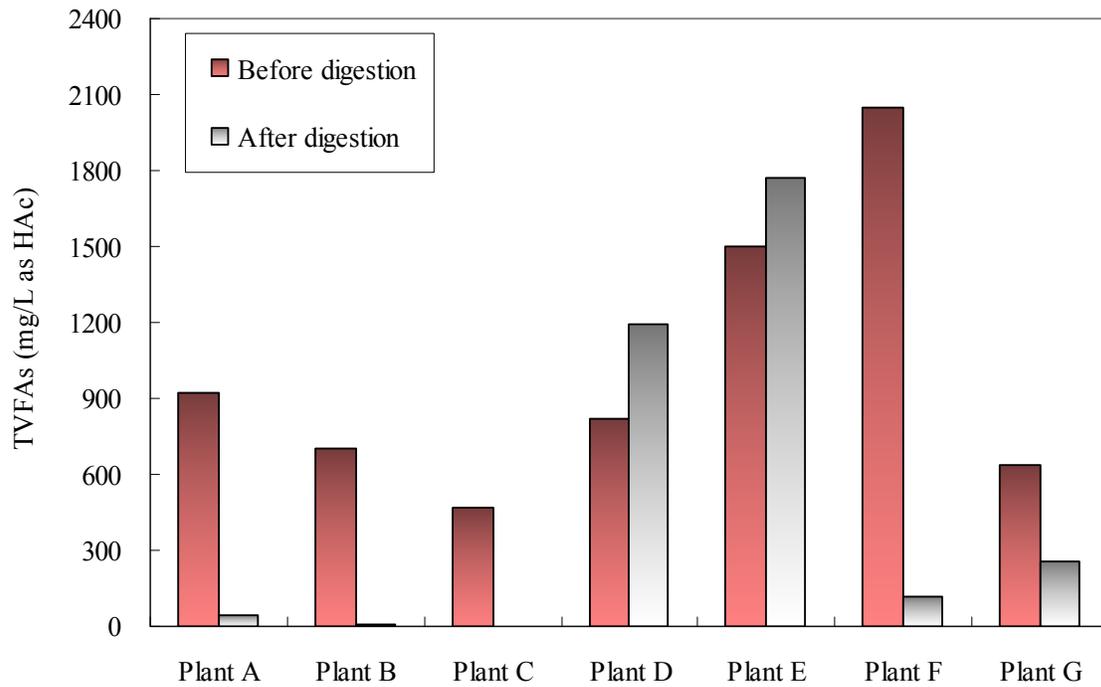
Figure A.4 − Total Volatile Fatty Acids as acetic acid before and after digestion adding

feed Iron to anaerobic digester for hydrogen sulfide control from seven municipal WWTPs.

Figure A.5 − Comparison of biogas generation of four different anaerobic digester feeds from seven municipal WWTPs.
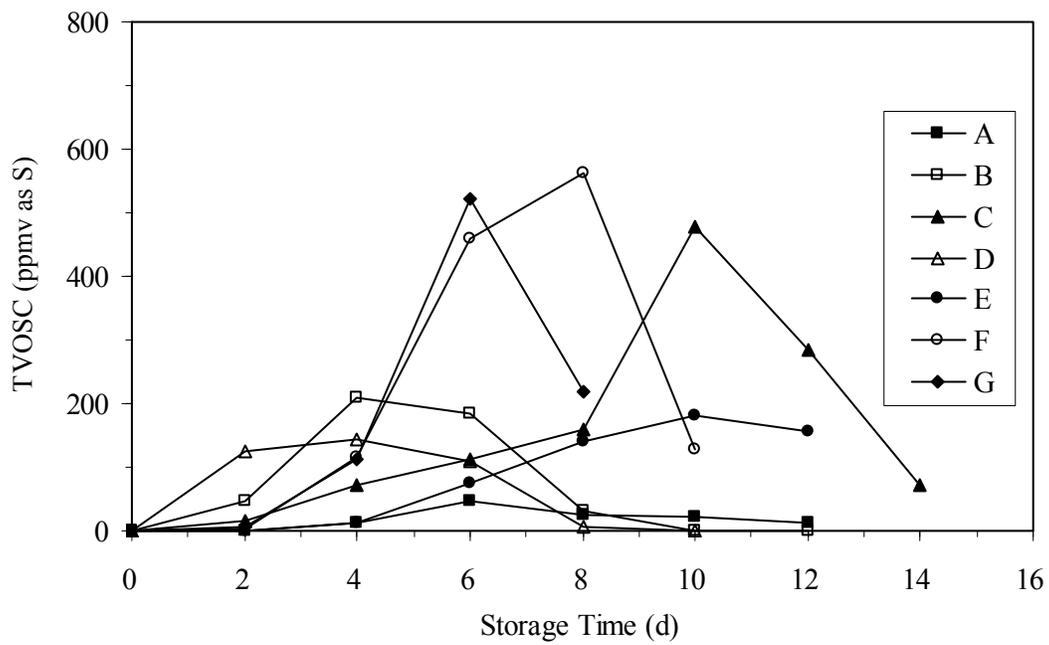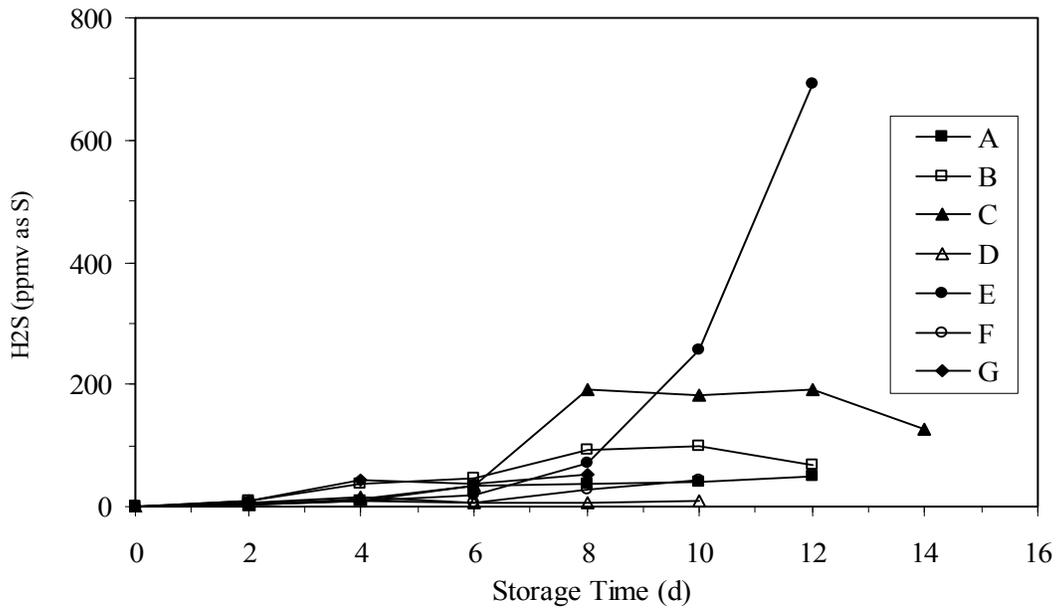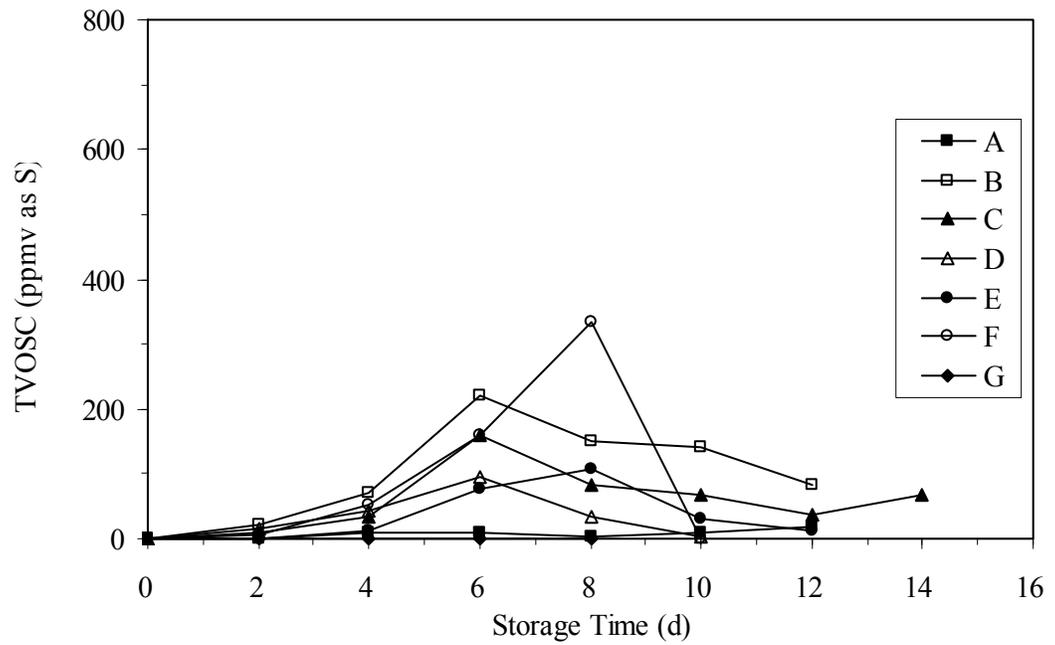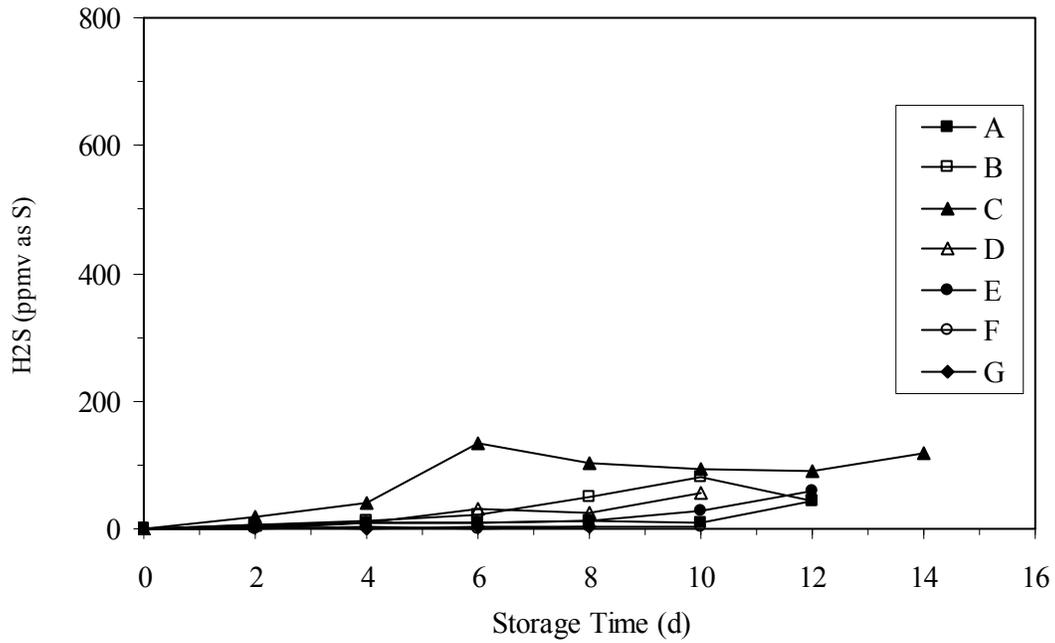
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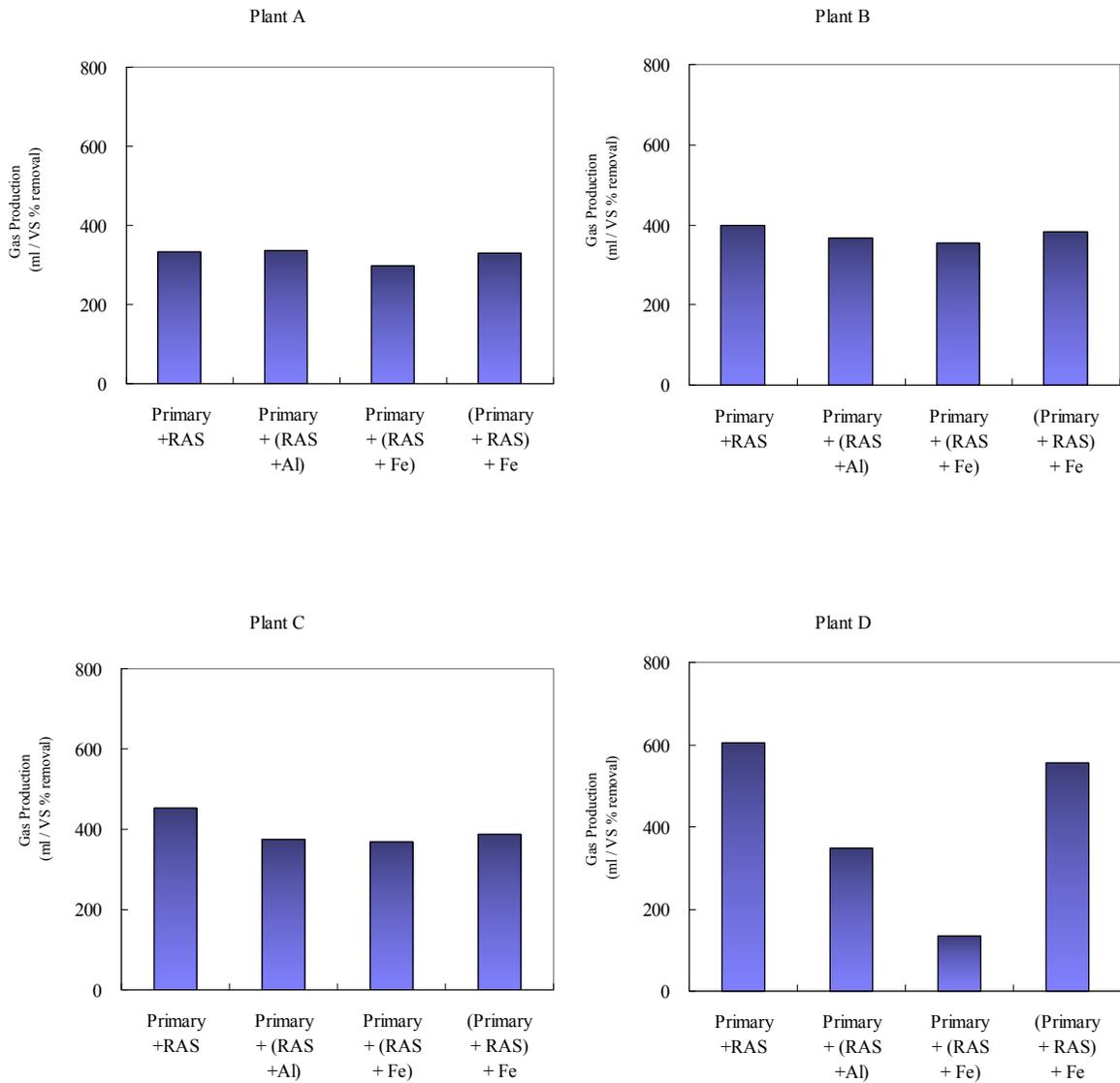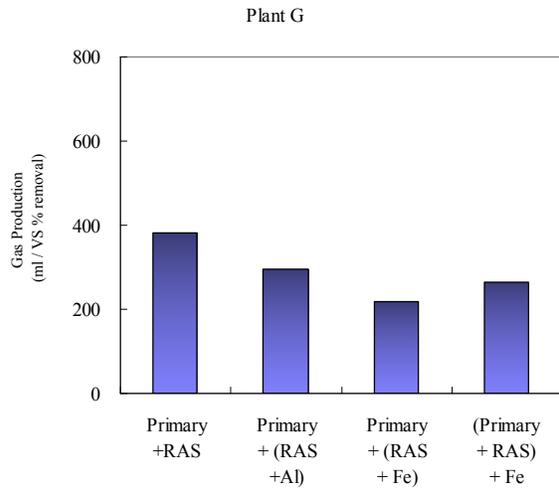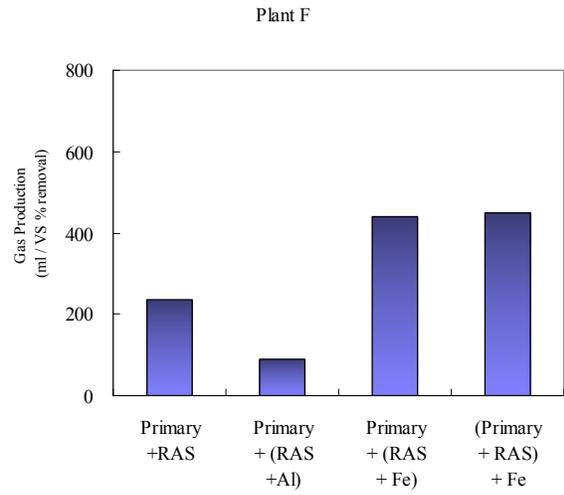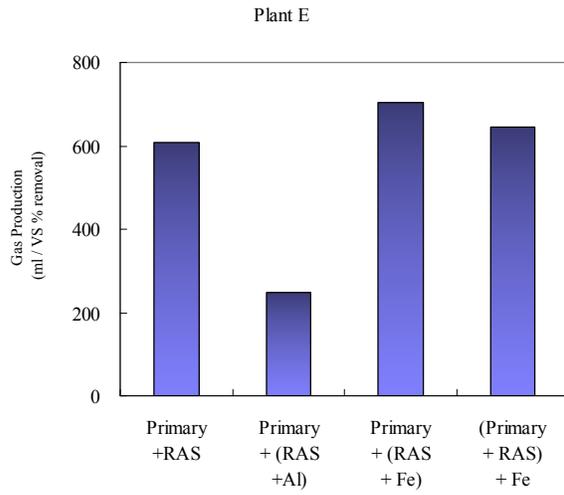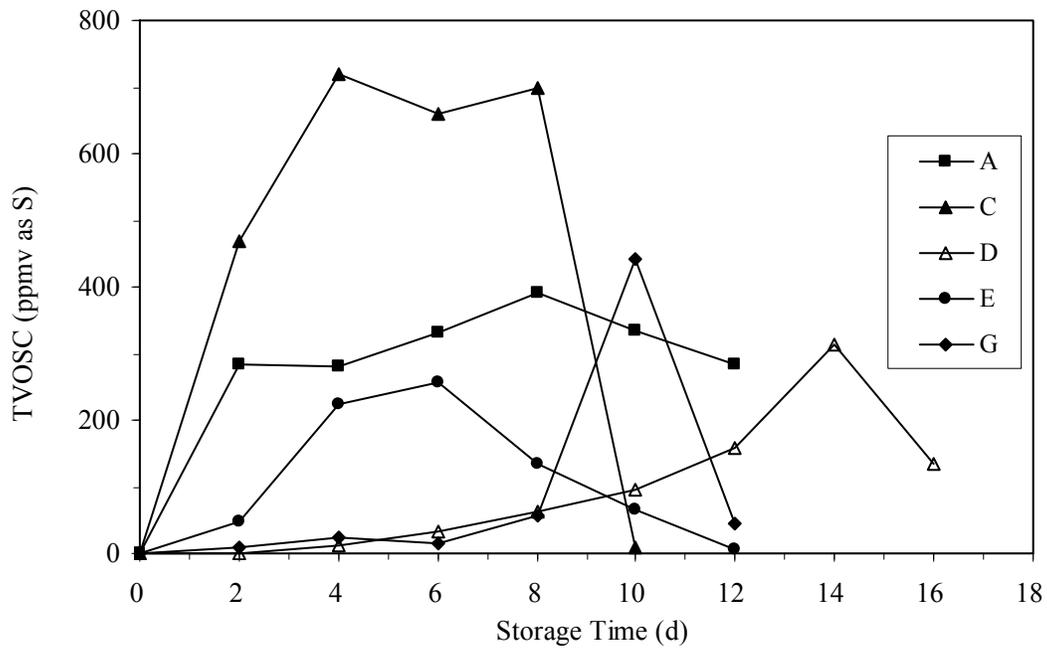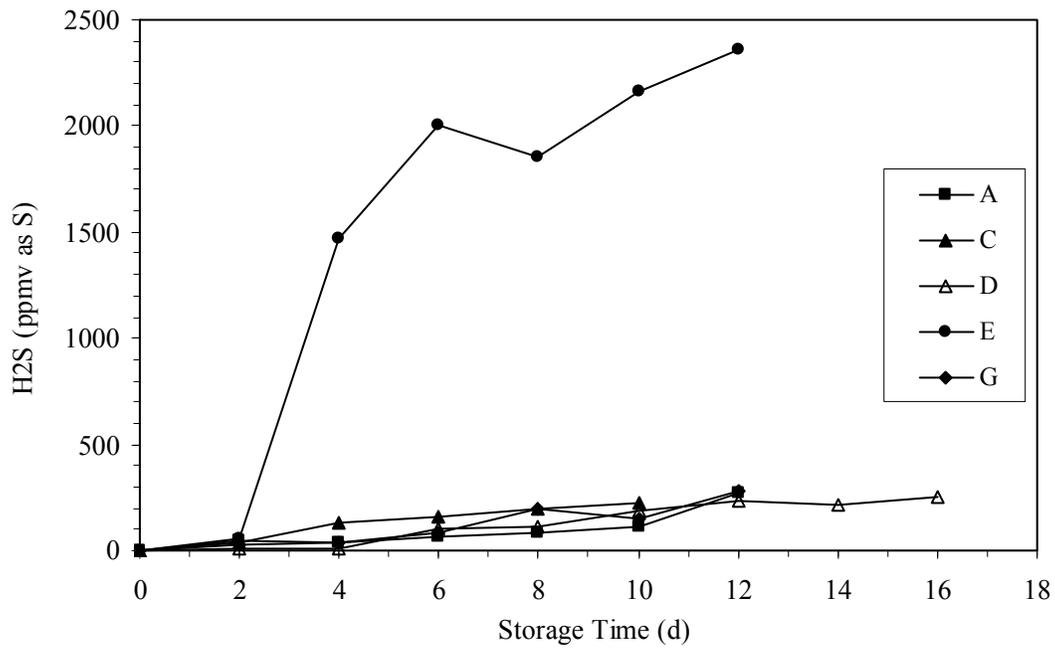
Figure A.6 − H2S and VOSCs concentrations of Field Digested Sludge from five municipal WWTPs.
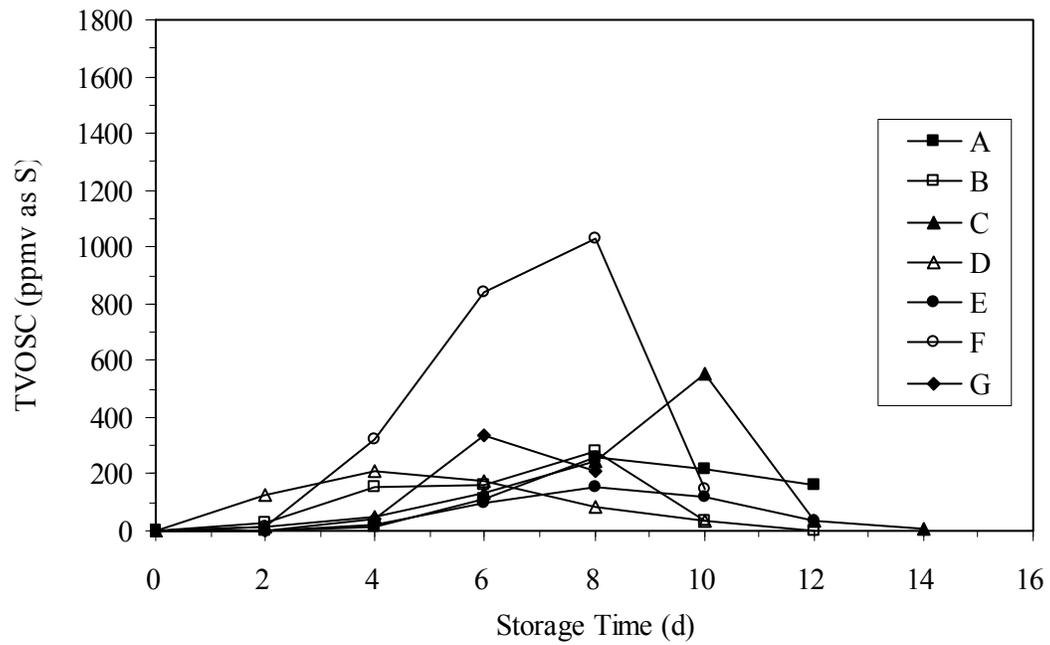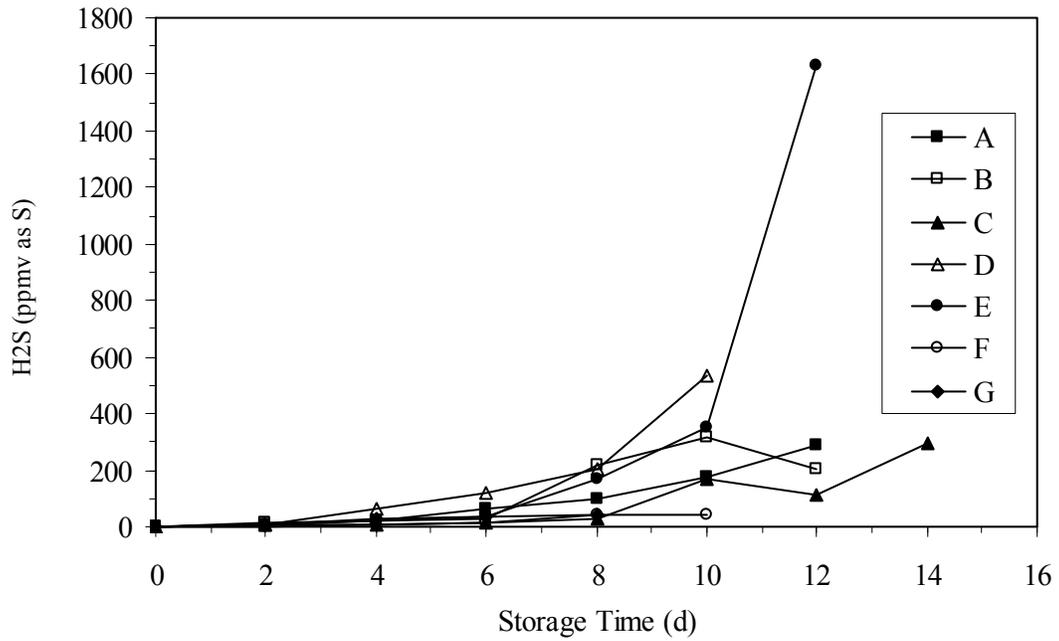
Figure A.7 − H2S and VOSCs concentrations of lab digested sludge adding Aluminum to RAS for phosphorus removal from seven municipal WWTPs.

Figure A.8 − H2S and VOSCs concentrations of lab digested sludge adding Iron to RAS for phosphorus removal from seven municipal WWTPs.

Figure A.9 − H2S and VOSCs concentrations of lab digested sludge adding feed Iron to anaerobic digester for hydrogen sulfide control from seven municipal WWTPs.