Sequential Anaerobic-Aerobic Digestion: A new process technology for biosolids product quality improvement

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(Abstract)

Anaerobic digestion is widely used for stabilization of solids in sewage sludges. Recent changes in the priorities and goals of digestion processes are focusing more attention on the efficiency of these processes. Increasing hauling cost and restrictions for land applications are two factors which are driving the increased attention to digestion efficiency. Noxious odor production from the land applied biosolids is another important issue related to digestion efficiency. Existing anaerobic digestion or aerobic digestion processes failed to provide simultaneous solution to biosolids related problems i.e. simultaneous VS reduction, better dewatering of biosolids and lesser odors from the biosolids.

Studies done by Novak et al. (2004) using different activated sludges show that anaerobic-aerobic digestion and aerobic-anaerobic digestion both increase volatile solids reduction compared to a single digestion environment. They proposed that there are 4 VS fractions in sludges: (1) a fraction degradable only under aerobic conditions, (2) a fraction degradable only under anaerobic conditions, (3) a fraction degradable under both anaerobic and aerobic conditions, and (4) a non degradable fraction. It has also been found (Akunna et al., 1993) that anaerobic-aerobic sequential treatment of wastewater can help in achieving substantial nitrogen removal. These results suggest that sequential anaerobic-aerobic digestion can address multiple biosolid related problems.

This study was designed to understand the effect of sequential anaerobic-aerobic digestion on the properties of resulting effluent biosolids. The study was carried out in two operation phases and during both phases one digester was maintained at thermophilic conditions and the other at mesophilic temperature conditions. In first operation phase (Phase-I) thermophilic digester was operating at 20 day SRT and mesophilic anaerobic digester was at 10 day SRT. The aerobic digesters following anaerobic digesters were operating at 6 day

SRT. In second operation phase (Phase-II), both thermophilic and mesophilic anaerobic digesters were operating at 15 day SRT and both had two aerobic digesters operating in parallel at 3 day and 6 day SRTs.

In addition, batch experiments were also conducted to measure the performance of aerobic-anaerobic digestion sequence. Another study was carried out to understand the nitrogen removal mechanism during aerobic digestion of anaerobic digested sludge. The feed sludge was spiked with four different concentrations of nitrate and nitrite.

It was observed during the study that aerobic digestion of anaerobic sludge helps in achieving higher Volatile solid reduction (~65% vs ~ 46% for mesophilic digestion and ~52% for thermophilic digestion). This result supports the hypothesis concerning the different fractions in volatile solids. Experimental results also show that the increase in VSR upon increasing anaerobic digestion SRT (more than 15 days) is less than the increase in the VSR due to the same increment of aerobic digestion SRT. Reduction in COD and VFA were also measured to be more than 50% during aerobic digestion.

Investigation of nitrogen fate during the sequential anaerobic-aerobic digestion show more than 50% total nitrogen removal. Higher nitrogen removal was in thermophilic anaerobic – aerobic digester combination than that in mesophilic anaerobic–aerobic combination. The most probable reason for the removal was simultaneous nitrification and denitrification. Higher concentration of readily available VFA from thermophilic anaerobic digested sludge provide advantage in denitrification in following aerobic digester.

The resulting biosolids produced during sequential digestion process were also analyzed for dewatering properties and odor production. Proteins and polysaccharides concentrations were observed to decrease during aerobic digestion for thermophilic anaerobic - aerobic digestion combination, while in another combinations polysaccharide concentrations increases at aerobic phase with 3 day digestion. The concentration of polysaccharides decreases at higher digestion period of 6 and 9. The result of decrease in polysaccharide and protein was

reflected by the reduction in the polymer dose consumption and decrease in the optimum CST for the biosolids resulting from the sequential anaerobic aerobic digestion.

Experimental results from odor experiments show that odor production potential of the biosolids decreases with increase in both anaerobic phase SRT and aerobic phase SRT. Thermophilic biosolids produces comparatively low odors but for longer periods, while mesophilic biosolids produces higher magnitude of odors during storage but only for comparative shorter period. Aerobic digestion of anaerobic sludge helps in reducing more than 50% odor production, but freeze-thaw cycle experiment shows that in both anaerobic and sequential anaerobic – aerobic digested sludges have higher potential for odor production. Higher aerobic digestion SRTs (6 days and above) shows more potential of reducing odors, but more experimental work is required to be done.

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Dedication

To my family...
My father for encouraging me to pursue my dream
My mother for inspiring in me, her love of all life, truth and education
My brother, grandparents and uncle for their unquestioned love and affection towards me

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List of Acronyms

SRT	Solid Retention Time
VSR	Volatile solids removal
Me-10	Mesophilic anaerobic digester operating at 10 day SRT
Me-15	Mesophilic anaerobic digester operating at 15 day SRT
MeAer3	Aerobic digester operating at 3 day SRT and receiving feed from mesophilic anaerobic digester
MeAer6	Aerobic digester operating at 6 day SRT and receiving feed from mesophilic anaerobic digester
MeAer9	Aerobic digester operating at 9 day SRT and receiving feed from mesophilic anaerobic digester
Th-15	Thermophilic anaerobic digester operating at 15 day SRT
Th-20	Thermophilic anaerobic digester operating at 20 day SRT
ThAer3	Aerobic digester operating at 3 day SRT and receiving feed from thermophilic anaerobic digester
ThAer6	Aerobic digester operating at 6 day SRT and receiving feed from thermophilic anaerobic digester
ThAer9	Aerobic digester operating at 9 day SRT and receiving feed from thermophilic anaerobic digester
Thermo (ThAer) series	Group of aerobic digesters receiving feed from thermophilic anaerobic digester
Meso (ThAer) series	Group of aerobic digesters receiving feed from mesophilic anaerobic digester
ORP	Oxidation reduction potential
CST	Capillary suction time
BESA	Bromoethane sulfonic acid
Fz Th	Freeze thaw

Chapter 1

Literature Review

1.1 Aerobic Digestion

Aerobic digestion is a process that stabilizes waste organic matter using oxygen as the terminal electron acceptor. During aerobic digestion, biodegradable particulate matter is hydrolyzed and converted into biodegradable soluble organic matter, releasing ammonia and phosphate. Organic matter is converted to carbon dioxide, water and active biomass by heterotrophic bacteria. The lysis: regrowth model using IAWQ ASM No.1 is the common models used to simulate the aerobic digestion process (Grady et al., 1999).

The volatile solid reduction during aerobic digestion depends on several factors including the temperature of the operation, solids retention time (SRT) and fraction of biodegradable solids in the solids (Grady et al., 1999). The operational temperature and SRT can be optimized to gain efficient solids removal, but the biodegradable solids fraction depends upon the source of wastewater and wastewater operational characteristics. The specific oxygen uptake rate (SOUR) and volatile solid removal (VSR) are two common parameters used to measure the degree of sludge stabilization by aerobic digestion (Eikum & Paulsrud, 1977). Aerobic digestion results in loss of both volatile suspended solids and fixed suspended solids. Degradation of biodegradable solids leaves higher amount of non-biodegradable stabilized solids (Eikum & Paulsrud, 1977 and Grady et al., 1999).

Aerobic digestion can be successfully used for digestion of solids with a high nitrogen content. Mulder et al (2001) found that optimization of temperature and SRT can achieve efficient oxidation of ammonia to nitrite and in subsequent stages, denitrification can be used for nitrogen removal from the system. Oxidation of ammonia leads to the loss of alkalinity during the process which will decrease the pH of the system so alkalinity addition may be required to maintain the

pH. A disadvantage of aerobic digestion includes inefficient destruction of pathogens at lower SRTs. Authothermal themophilic aerobic digestion (ATAD) can help in simultaneous volatile solid removal and pathogen destruction. A high concentration of solids (40,000 mg/L to 60,000 mg/L) is digested aerobically at 45-65 ^{o}C. Studies found no nitrification in the ATAD system, which leads to increase in pH due to ammonia accumulation (Grady et al., 1999). High concentrations of ammonia and high temperatures can result in inactivation of pathogens in the system. Contrary to these investigations, Kim et al (2004) and Mason et al (1992) suggested that aerobic digestion at thermophilic temperatures (more than 55 ^{o}C) can also remove nitrogen from solution by the action of a bacillus-like genre of micro-organisms. The low solubility of oxygen, foaming and poor dewatering are major problem associated with the ATAD systems (Grady et al., 1999).

1.2 Anaerobic Digestion

The anaerobic digestion process is a well established digestion process in the wastewater treatment industry. Mesophilic digestion (35 ^{o}C) is widely used for the digestion of municipal sludge. This can usually achieve more than 38 % volatile solid reduction as per requirement of 40 CFR 503 part (b) to achieve Class-B biosolids. The major disadvantage of the mesophilic digestion process is that it cannot achieve Class-A biosolids because the process fails to fulfill the time-temperature exposure criteria for pathogen destruction. Other digestion processes including the single stage thermophilic digestion and dual stage digestion processes have been considered and investigated to achieve the Class-A biosolids. The major advantage of Class-A biosolids is that they have flexibility in land application over Class-B biosolids. A subsequent section will provide the detail discussion of various anaerobic digestion processes and their advantages/disadvantages.

1.2.1 Anaerobic Digestion Fundamental

The anaerobic digestion process is thought to consist of 4 steps (see Figure I-1):

1. Hydrolysis,
2. Acidogenesis,
3. Acetogenesis, and

4. Methanogenesis.

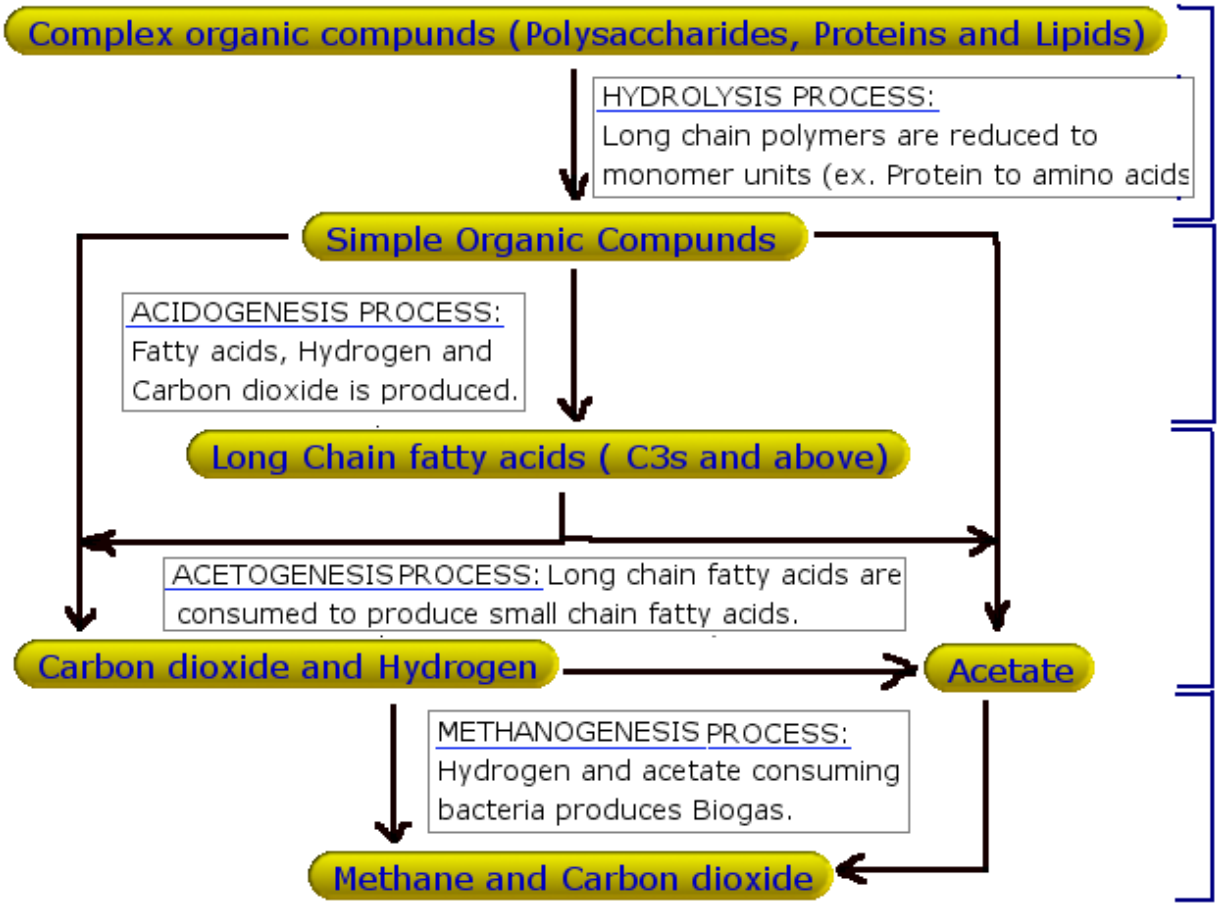

Figure I-1 - Overview of metabolic process and intermediate steps of solids digestions during the anaerobic digestion process.

Hydrolysis of organic rich waste and methanogenesis are the rate limiting steps (Gavala et al., 2003). During the first step of anaerobic degradation, complex organic matter of the sludge is hydrolyzed into smaller organic units (for example, Protein → Amino acids, Carbohydrates → glucose, Lipids → long chain fatty acids etc.). In the later phase of the degradation, VFA (volatile organic acids) are produced and during methanogenesis, CO_2, H_2 and acetate are consumed by micro-consortia for production of CH_4, CO_2 and cell mass.

1.2.2 Comparison between mesophilic and thermophilic digestion process

Mesophilic digestion (35 ^{o}C) is a widely accepted sludge treatment process in the US and Europe, but it has limitation in term of pathogen destruction. Due to the high pathogen presence in biosolids, regulation 40 CFR 503 part (b) limits the solid disposal options for the resulting biosolids. Investigations suggest that thermophilic digestion can achieve 3-log pathogen destruction with a minimum 10 day SRT, but at an additional cost of higher energy to elevate the temperature. Table I-1 lists the advantages and disadvantages of thermophilic digestion in comparison to mesophilic digestion.

Table I-1 - Advantages and disadvantages of thermophilic digestion process over mesophilic digestion (NOTE: Table prepared by using the references from various sources)

	Advantages	**Disadvantages**
1.	Log 3 pathogenic destruction	Higher energy requirement for the process operation
2.	More CH_4 production	Susceptible for ammonia inhibition and destabilization due to upset in the proximity of H_2 producers and consumers.
3.	Construction cost is less due to smaller reactor size is required to achieve equivalent VSR from Mesophilic digestion.	Produces higher VFA which are responsible for highly malodors effluent.
4.	Degrade higher amount of VS and protein.	Higher protein degradation leads to the production of NH_4^+ and NH_3 which may toxify the system. Also protein degradation release sulfur based amino acids which generate H_2S and other organic sulfur based gases in the system and resulting biosolids.
5.	More resistant against foaming.	
6.	Ability to treat high organic load with low yield.	

1.2.3 VFA Degradation

Meon et al (2003) during their comparative study of thermophilic and mesophilic digestion found that mesophilic digestion produces less VFA and that the VFA concentration increases with a decrease in the SRT of the digestion process. It has been found that acetic acid is the major volatile acid, being 4-5 times higher than other volatile acids. Their studies also suggest that upon decreasing the SRT of the digestion process, propionate, butyrate and valeric acids accumulate rather than acetic acid.

Low VFA levels are critical for the stability of the anaerobic digesters especially thermophilic digesters. During methanogenesis, the proximity of H_2-producing and H_2-consuming microbes is important for maintaining a low H_2 concentration in the digester (Parkin and Owen, 1986). In the absence of microbial proximity, the pH gets reduced leading to an increase in propionate and butyrate. Higher chain fatty acids are not the preferred substrate for methanogenesis and further drop the pH destabilizing the whole anaerobic digestion process (Wang et al., 1999).

1.3 Multi-stage digestion processes

Single stage digestion processes including aerobic and anaerobic digestion have the disadvantage that the input of new feed recontaminates the sludge with pathogens. Therefore, designers have used multistage digestion processes to achieve higher VS reduction and achieve higher pathogenic reduction. To achieve higher VS reduction and process stability, digestion stages are designed to exploit the benefits of different genre of microbial communities. Most common microbial communities considered in the process design are acetogens, methanogens, thermophilic microbes and mesophilic microbes for anaerobic digestion process and heterotrophic microbes for aerobic digestion. The major focus for multistage digestion has been on the acid-gas phased digestion (A/GPD) and temperature phased anaerobic digestion (TPAD) processes. Studies by Tapana et al (2000a, b)**,** and Park et al (2004) also looked into the effect of pre- and post- aerobic treatment of anaerobic digested sludge. In a subsequent section, anaerobic/aerobic treatment will be reviewed.

1.3.1 Acid-gas phased digestion

Pohland & Ghosh (1971) first proposed acid-gas phased digestion (A/GPD). In the first stage of digestion, a low pH is maintained by using low SRT and a high organic load. The low pH condition favors the growth of acetogens and at SRTs as low as 12 hrs to 2 days, methanogens are washed out. The second phase, which has higher a SRT (15 to 20 days), is more suitable for methanogenic growth.

The principal advantage of A/GPD is the ability to optimize hydrolysis and acidogenesis reactions in the acid reactor and acetogenesis and methane formation in gas phase digester. Other documented advantages of A/GPD are –

1. More effective for handling organic shock loads (Fox and Pohland, 1994), and
2. Acid stage digesters can help in detoxifying the influent which may otherwise cause harm to the methanogens, providing a more stabile system in comparison to the single stage digestion.

1.3.2 Temperature phased anaerobic digestion (TPAD)

The TPAD process utilizes the benefits of thermophilic and mesophilic organism during the different digestion phases of the process. In the TPAD process, the thermophilic stage has SRT in the range of 3-5 days and the mesophilic stage has SRT range of 15 to 20 days (Dichtl, 1997). The higher temperature and higher SRTs of the first stage helps to overcome the shortcomings which are present in single stage digestion processes and A/GPD process as well.

Studies conducted by Inman et al (2004) and Han & Dangue (1997) showed that the TPAD system can achieve higher volatile reduction than mesophilic digestion and it can produce higher amount of methane than single stage mesophilic digestion. Vandeburgh & Ellis (2002) showed that the TPAD process is capable of tolerating higher nitrogen loads.

1.3.3 Aerobic pre- /post- treatment of anaerobic sludge

Aerobic pretreatment and post treatment of anaerobic sludge has been considered by only few researchers. This combination has been found to produce results superior to conventional mesophilic digestion in term of dewatering, odor generation and VS reduction. Tapana and

Pagilla (2000a, b) during their investigation of pre and post thermophilic-aerobic treatment of anaerobic sludge found VS reductions up to 65% with an aerobic digester SRT as short as 1 day. These researchers found improved dewatering properties for both pre and post treatment in comparison to conventional mesophilic digester. In another study, Tapana and Pagilla (2000b) found a VS reduction of 61% for swine sludge as well.

Novak and Park (2004) carried out batch digestion to investigate the effect of pre- and post-treatment of aerobic digestion on anaerobic sludge. They found that for similar digestion SRTs under mesophilic conditions, both pre- and post- treatments achieved the same 60% VS reduction. They also suggested that aerobic pretreatment of WAS leads to the formation of nitrate which may impede the anaerobic digestion process. During the aerobic-anaerobic digestion tests, glucose was added during the anaerobic digestion phase to consume the nitrate produced in the initial aerobic digestion phase. Their study also suggests that the organic material in sludge can be categorized as:

1. Only anaerobically digestible material.
2. Only aerobically digestible material,
3. Material which can be digested by both anaerobic and aerobic digestion process, and
4. Non-digestible material.

Subramanian (2005) during her studies found that sequentially digested sludge (anaerobic-aerobic digestion sequence) results in a low CST while anaerobic digested sludges have CST approximately 10 times higher. In addition, anaerobically digested sludge consumes a higher polymer conditioning dose in comparison to anaerobic-aerobic sequentially digested sludges. Her results showed that specific resistance to filtration (SRF) for thermophilic anaerobic sludge followed by aerobic digestion decreases more than 50%, while for sequential mesophilic anaerobic–aerobic digestion the decrease is less than 25%. She also found that upon sequential anaerobic-aerobic digestion, the bound water content of the resulting biosolids also decreased substantially.

1.4 Waste-activated sludge and the role of cations

Waste-activated sludge contributes a substantial amount of solids and the digestion of the material in sludge floc has been found to be associated with cations present in the floc matrix (Park et al, 2005). Novak & Higgins (1997), Novak et al (2003) and Park et al (2004) found that the major cations associated with the sludge floc are sodium, potassium, calcium, magnesium, iron and aluminum. Frølund et al (1996) proposed a sludge floc model in which a floc consists of micro-consortia embedded in matrix of biopolymers including proteins, polysaccharide, DNA and humic acids. These biopolymers are bound in the sludge matrix and are associated with different cations. During aerobic digestion, divalent cations accumulate in the solution resulting from the release of lectin-like proteins which are then degraded. Higgins and Novak (1997), and Novak et al (2003) suggest that lectin-like protein is bound in the sludge floc matrix along with polysaccharide. The polysaccharides concentration increases during aerobic digestion because of cessation of polysaccharide degrading enzyme's activity (Novak et al, 2003). During anaerobic digestion, ferric bound biopolymer is released upon the reduction of Fe(III) to Fe(II) and is degraded (Park et al, 2004).

Movovalent cations are considered to deflocculate activated sludge floc, while multi-valent cations are found to stabilize the floc matrix (Novak and Higgins, 1997; Murthy and Novak, 1999). Kakii et al (1985) in their study, found that aluminum and ferric cations have higher valency and lower solubility than any other type of cations and hence play more critical role in floc formation. It has also been documented that iron has a strong tendency to get bound along with proteins. The role of aluminum is considered equally important in the sludge. It is found to coagulate polysaccharides and humic acids from the solution, but little information is available about the role of aluminum associated biopolymer.

1.5 Odor production in biosolids

Odor production from the digested biosolids is one of the major problem utilities are trying to solve. Odor restricts biosolids disposal options for the utilities and increases the cost of biosolid handling. Studies carried out by Muller et al (2004) and Novak & Murthy (2002) suggest that

centrifugation of biosolids along with polymer addition shear the sludge solids and makes additional biopolymer available for microbial degradation. They also suggest that biosolids produced using a belt filter press will produce less odors in comparison to that from a centrifuge.

Digested biosolids have high protein in solution and contain undigested volatile solids which can serve as good food source for anaerobic microorganisms. During biosolids storage, anaerobic conditions persist and the protein is broken down into cysteine and methionine followed by production of methanethiol, which is then converted to sulfide by methanogenic bacteria. Other gases which are considered to contribute towards the odors from the biosolids are dimethyl sulfide (DMS) and dimethly disulfide (DMDS). Higgins et al 2002 and Lomas et al (1999a, b, c and 2001) suggest that sulfur based gases are either consumed or get demethylated by set of other bacteria present in the biosolids. Methanogenic consortia are found to be more active under anaerobic conditions for cycling sulfur based gases. Higgins et al (2003) summarized the cycling of sulfur based odor causing gases as a set of interconnected reactions. It was suggested that methyl mercaptan can be methylated form to dimethyl sulfide or it can be oxidized to dimethyl sulfide. Demethylation of dimethyl disulfide produces dimethyl sulfide, which on demethylation produces hydrogen sulfide. Methionine, cysteine, and sulfate are the substrate for the used by microbes for the energy generation.

Verma (2005) found that the iron content in the sludge was correlated with the odor generation from the anaerobically digested biosolids. A strong correlation between VS reduction by anaerobic digestion and the iron content of the sludge has been found by Park et al (2005) supporting the role of Fe reduction during anaerobic digestion. In another study (Verma, 2005), the effect of the anaerobic digestion SRT has been investigated and investigators found that the peak organic sulfur concentration in digester headspace as well as biosolid cake decreases with an increase in the digester SRT. Methanogens in the biosolids can reduce the odor by consuming organic sulfur compounds and producing H_2S, which later precipitate out as FeS if sufficient iron is present in biosolids (Novak et al, 2005).

Another factor which has been found associated with excess odor from the sludge has been freezing followed by thawing. When biosolids are applied on the land after dewatering process, they under go freeze-thaw process during the seasonal cycle and it has been reported that after freeze-thaw cycle biosolids produce more odors (Personal communication with S. Murthy). Freeze-thaw has been investigated for the purpose of sludge conditioning because it enhances sludge dewatering, reduces sludge bound water (Lee and Hsu, 1994) and transforms the floc structure into a more compact form (Vesilind et al, 1991, Kawaski and Matsuda, 1995). Lee et al (1999) also found that instant freezing the sludge has no effect on microbial activity reduction. This suggests that microbes will be able to recover as soon as the sludge is thawed and they will use the bioavailable protein for growth resulting in odor generation from the biosolids.

1.6 Nitrogen removal

Treatment of sludge having a high nitrogen content has always been a difficult task, especially for anaerobic treatment because ammonia can inhibit microbes that are active in this process (Hansen et al, 1997 and Sung et al, 2003). Aerobic treatment has been mainly considered for the treatment of sludge that contains higher influent nitrogen, but challenges still remains due to the inhibition of nitrification by free ammonia and nitrous acid. Bhargava and Datar (1988) reported that the optimal temperature for the nitrification is between 25-30 degree C and maximum nitrification is achieved at 30 degree C. The optimal pH range for both steps of nitrifications is between 6 and 8. It has been suggested that at thermophilic conditions little or no nitrification will occur due to inactivation of nitrifying organisms (EPA, 1990), but Kim et al (2003) found that in thermophilic aerobic digestion nitrogen removal can be achieved. They found that 91% nitrogen removal can be achieved with an HRT of 3 days and temperature ranging from 50 to 70 ^{o}C. In another study Kim et al (2004) found that the Bacillus genre of microbial community is more important in removal of ammonia from a thermophilic aerobic digester. They also found that 29% nitrogen removal took place due to nitrogen gas formation due to deammonification. N_2O is also found in the gas mixture suggesting a biologically assisted nitrogen reduction process.

Another study carried out by Akunna et al (1994) showed aerobic post treatment of anaerobic digested effluent can achieve another 30% COD removal and 70% nitrogen removal in the effluents. Another result from the same study suggests that carbon and nitrogen removal in sludge is a result of aeration rate and the recycle-to-influent ratio. Recycling of the sludge also has been found to impact the methane production in the anaerobic treatment phase as well (Akunna et al, 1994). Systems having higher organic load are more suitable for the heterotrophic bacteria which out compete autotrophic nitrifiers that lead to nitrification inhibition. Pollice et al (2002) investigated the effect of sludge age and aeration on oxidation of ammonia to nitrite. The results indicate that the sludge age is critical parameter for partial nitrification when the oxygen supply is not limiting. The oxidation of ammonia to nitrite was successfully achieved during a sludge retention time of about 10 days. The ratio of nitrite to nitrate depends upon the SRT due to difference in the growth rate of ammonia oxidizing bacteria and nitrite oxidizing bacteria. Nitrite oxidizing bacteria have slow growth rate, hence nitrate production is lower than nitrite production from the oxidation of ammonia (Hellinga et al, 1998).

1.7 Summary and Study objectives

The literature review and work done in the environmental laboratories of Virginia Tech suggests that either of anaerobic or aerobic digestion process alone cannot achieve all desired qualities (higher VS reduction, better dewatering, and low order production) in resulting biosolids. Anaerobic digested sludges are stable and have low volatile solids, but they have poor dewatering which increases the polymer demand & hence operation cost. They also produce higher sulfur odor which limit the disposal options. Aerobic sludge show comparative better dewatering but have low pathogen reduction potential as compared to anaerobic digested sludge.
The concentration of influent nitrogen in the digesters is also a limiting factor in the selection of a digestion process. The size of wastewater treatment utilities and financial constraints are other aspects that control the design of digestion processes. The results from the recent studies suggest that combination of anaerobic-aerobic digestion processes may help in producing better biosolids. This study aims to investigate the performance of anaerobic-aerobic digestion by studying –

1. The effect of anaerobic and aerobic SRTs on VS reduction,

2. Nitrogen removal in the aerobic digesters,
3. Effect of anaerobic phase temperature on the nitrogen removal,
4. Change in the dewatering properties upon aerobic digestion of anaerobic effluent, w.r.t. to dewatering of only anaerobic digested effluent,
5. The effect of aerobic digester on the odor generation from resulting biosolids and effect of aerobic SRTs on the odor production, and
6. The effect of freeze-thaw on the odor production.

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Chapter 2

Efficient Nitrogen removal and volatile solid reduction in sequential anaerobic-aerobic digestion process

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Abstract

Sequential anaerobic–aerobic digestion has been studied for use in wastewater treatment, but has had limited use for digestion of waste solids. Recent studies suggest that some solids in sludge are degraded only during anaerobic digestion and some only during aerobic digestion. Therefore, dual digestion (anaerobic/aerobic) is expected to provide additional volatile solids reduction beyond that which can be achieved by either anaerobic or aerobic digestion alone. In this investigation, dual digestion was compared with single stage anaerobic digestion using both mesophilic (35^0C) and thermophilic (55^0C) digestion. The results show that dual digestion was able to achieve more than 60% VS reduction, compared to 46% and 52% by mesophilic and thermophilic digestion, respectively alone. Aerobic digestion SRTs of 3, 6 and 9 days were studied and increased VS reduction was observed for all aerobic detention times. This study also shows that more than 50% total nitrogen could be removed from the anaerobic effluent after digesting at aerobic conditions.

Keywords – Thermophilic digestion, Mesophilic digestion, sequential anaerobic-aerobic digestion, nitrogen removal, denitrification, ammonia stripping, and TKN removal.

2.1 Introduction

Biosolids management is one of the important aspects for the wastewater treatment utility because of financial and health and safety issues. The cost of biosolid hauling is a major expenditure for wastewater treatment utilities. Pathogens and odor problems may restrict the

biosolid disposal options and affect hauling cost. Biosolids applied to land can also impact ground water quality, primarily through nitrogen contamination. Mesophilic (35 ^{o}C) anaerobic digestion is one of the common solid stabilization processes for removal of volatile solids and COD. Utilities that have high influent organic nitrogen content may prefer to use aerobic digestion due to the inhibition of the anaerobic process by ammonia. Both conventional aerobic and anaerobic digestion processes at mesophilic temperature have disadvantages, including the inability to achieve desired pathogen reductions, poor dewatering and odor production. Operations at thermophilic temperature are relatively more prone to destabilization, but have potential of producing class-A biosolids.

Ghosh and Pohland (1971) studied dual phase digestion processes (acid/gas phased digestion, A/GPD, and temperature phased anaerobic digestion, TPAD) and found that dual phase digestion processes can perform better than single phased digestion. A/GPD and TPAD both provide stable digestion and can tolerate comparatively high concentrations of ammonia and other toxins. These digestion processes provide higher VS reduction, more methane production and higher pathogen reduction, however they have the disadvantages of poor dewatering and high odor production. Another major disadvantage of anaerobic digestion is the high concentration of nitrogen in the digested sludge and subsequent centrate produced during dewatering. Recycle of centrate back to the head of the plant add a high ammonia-nitrogen load into the system.

Tapana et al (2002) investigated an anaerobic and aerobic digestion combination to treat swine waste, to determine the effect of pre and post aerobic treatment of anaerobic digestion. They found that with both thermophilic aerobic- mesophilic anaerobic combination and mesophilic anaerobic–thermophilic aerobic digestion a higher load of nitrogen could be treated with comparatively better dewatering properties and higher VS reduction. Both combinations have been found to meet the class-A requirements for pathogen reduction. The study suggested that one day of aerobic digestion can be sufficient to achieve the desired treatment goals. Subramanian (2005) also found improved dewatering and low polymer conditioning requirement for sequential anaerobic-aerobic digested biosolids.

Novak et al (2003) found that during anaerobic and aerobic digestion of waste activated sludge (WAS), VS reduction was due to the degradation of different portions of the floc matrix. Novak and Higgins (1997) proposed a floc structure in which proteins and polysaccharides are bound to each other with divalent cations (calcium and magnesium). The proteins observed were similar to lectin and during aerobic digestion this lectin-type protein gets degraded releasing divalent cations and polysaccharide in the solution. Polysaccharide degradation was not substantial and it was found that during aerobic digestion polysaccharide degrading enzymes are inhibited. Park et al (2004) has shown that anaerobic digestion of WAS degrades iron bound protein. Both these studies together suggest that different fractions of volatile solids exit. Only particular types of fractions are degraded during anaerobic and aerobic digestion processes.

Another important aspect of the anaerobic-aerobic sequential digestion process is removal of nitrogen. Akunna et al (1994) showed that aerobic post treatment of anaerobic digested effluent can achieve another 30% COD removal and 70% nitrogen removal. The investigators show that at a low COD/N ratio, nitrogen is lost from the system as N_2 and N_2O. Hanaki et al (1992) reported that pH, dissolved oxygen (DO) and short detention time are the other factors that affect N_2O formation during denitrification.

Sequential anaerobic-aerobic digestion has the potential for improving digestion of waste sludges and reducing the nitrogen in recycle streams. The objectives of this investigation were to evaluate the performance of sequential anaerobic-aerobic digestion in detail, including:

1. The effect of anaerobic and aerobic phase digestion detention times on the volatile solids reduction,
2. The effectiveness of the nitrogen removal process in two phase anaerobic-aerobic digestion, and
3. The effect of the anaerobic phase temperature (mesophilic versus thermophilic) on nitrogen removal in aerobic phase.

During this study one of the thermophilic digester performed poorly and provide the opportunity to study the effectiveness of aerobic digestion when the first stage anaerobic digestion process malfunctioned.

2.2 Material and methods

2.2.1 Bioreactor operation:

The study was divided into two phases as shown in Table II-1, along with the acronyms used in the discussion of the results. In Phase-I, the mesophilic anaerobic digester was operated at 10 days followed by 6 days of aerobic digestion and the thermophilic digester was operated at 20 days, with a 6 day aerobic digestion period. In the Phase-II, both anaerobic digesters were operated at 15 day SRT and two aerobic digestion periods were used, 3 days and 9 days. The aerobic digester temperatures were maintained at 30 ^{o}C. All digesters were maintained in a constant temperature room.

Table II-1 - Digester combination during two phases of study and acronyms of the digesters used during result analysis

Study phase	**Combination – 1 (SRTs)**		**Combination – 2 (SRTs)**	
	Thermophilic anaerobic digestion (55 C) - Stage 1	**Sequential Aerobic digestion (30 C) - Stage 2**	**Mesophilic anaerobic digestion (35 C) - Stage 1**	**Aerobic digestion (30 C) - Stage 2**
I	20 days (Th-20)	6 days (ThAr6)	10 days (Me-10)	6 days (MeAr6)
II	15 days (Th-15)	9 days (ThAr9)	15 days (Me-15)	9 days (MeAr9)
		3 days (ThAr3)		3 days (MeAr3)

Anaerobic digesters were fed with a mixture of gravity thickened primary sludge and dissolved air flotation thickened waste activated sludge (DAFT-WAS) 1:1 by weight. The solids percentage in the feed was maintained at 4%. Both primary and secondary sludge were provided by the Blue Plains wastewater treatment plant operated by the District of Columbia Water and Sewer Authority (DCWASA) on weekly basis by overnight shipment. The feed was stored in a 4

^{o}C room until used. Sludge was fed to the anaerobic digesters once per day and an equivalent volume of digested sludge was removed from the digester. The anaerobic digested effluent was fed to the aerobic digesters, maintaining the volume of the digester to keep the SRT constant. Figure II-1 shows the mass-flow and stage set-up of anaerobic-aerobic sequential digestion process.

For anaerobic digestion, plastic conical (egg-shaped) fermenters manufactured by Hobby Beverage Equipment Company were used. Anaerobic digesters were mixed by re-circulating gas from the headspace to the bottom of digester using Cole-Parmer 6-600 RPM variable speed pumps (operated at 40% of their maximum possible speed). No extra heating was provided for maintaining the temperature of the mesophilic digester, but for thermophilic digestion, hot water at 63 ^{o}C was circulated through poly-vinyl pipe around the periphery of thermophilic digester and the system was wrapped in insulating material to avoid heat loss. Gas produced during the digestion process from anaerobic digesters was collected in airtight Tedlar gas bags (Fisher Scientific) and periodic measurement of the gas volume and gas content was carried out. Due to the high operating temperature, water evaporated from the thermophilic digester and it was captured using a water trap. The average water loss was 50 ml per day and this water was reintroduced in the digester daily.

Aerobic digestion was carried out in stainless steel digesters provided by Blinchmann Engineering, except for digestion carried out at the 3 day SRT. For the 3 day aerobic digester, 9 L glass digesters (Fisher Scientific) were used due to the small operation volume (only 3 L). For aerobic digestion, mixing was achieved using external pumps (Cole Parmer, 6-600 RPM) and for aeration, air was supplied from a compressor and aeration-stones were used for oxygen transfer. Water was lost from the aerobic digesters due to evaporation and this water was replaced each day by adding distilled water prior to the sampling and wasting the effluent from the digesters. The dissolved oxygen level in all of the digesters was maintained at 3.0 ppm using flow regulating values.

Sample collection was initiated after two detention times of the anaerobic digesters. Solid (TS and VS), pH, Total Kjeldahl Nitrogen (TKN) and total ammonia was measured in the feed, anaerobic effluent and aerobic effluent on the same day. For volatile fatty acids (VFA), ions, soluble proteins and polysaccharides samples were centrifuged at 10,000 g for 20 min at 25 ^{o}C, filtered using 1.5 um cellulose filters (Type 934-AH, Whatman) followed by filtration using 0.45 um nitrocellulose filters (Fisher Scientific), and finally stored frozen until the analysis was conducted. Samples for total COD measurement were acidified using concentrated H_2SO_4 to fix the carbon.

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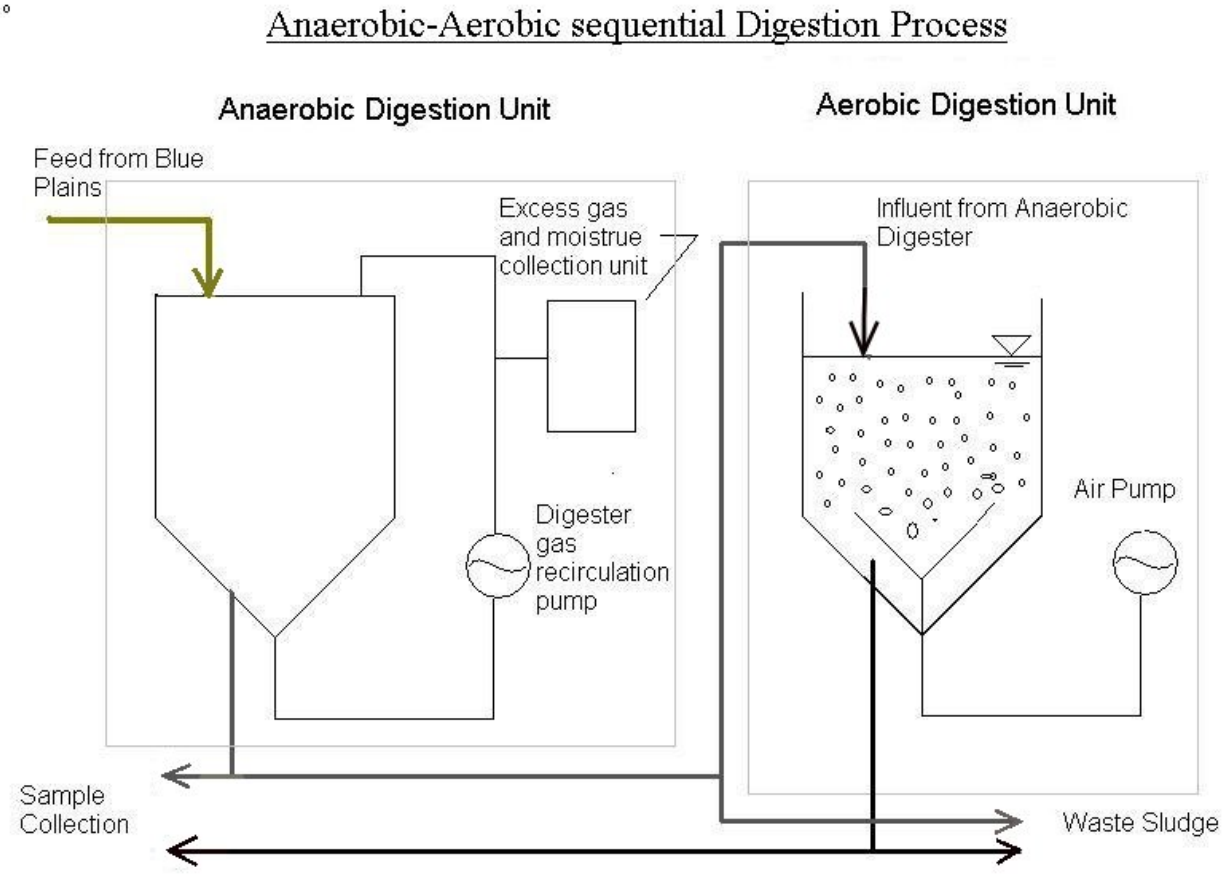

Figure II-1 – Typical digestion sequence and configuration of digesters used in the study of anaerobic-aerobic digestion process. Arrows represent the direction of the mass flow.

2.2.4 Analytical methods:

For determining the performance of the digesters, total solids, volatile solids in and out of each digester were measured according to Standard Methods for the Examination of Water and Wastewater (Standard Methods) (APHA 1999). Gas production, percentage gas distribution, pH, DO, digester temperature, chemical oxygen demand (COD), Total Kjeldahl Nitrogen (TKN), ammonia, selected dissolved ions and volatile fatty acids (VFA) measurements were done according to standard methods (APHA, 1999). DO, pH, solids percentage measurement were conducted on alternative days, while TKN and ammonia concentrations were measured once a week. The COD was measured on 5 samples collected during each operation phase.

The gas volume was measured every alternative day while emptying the gas bags and gas content measurements were done once a week. Gas volume measurements were made with a gas flow sensor (McMillan Co., 100T), coupled with an analog input process meter (with totalizer feature). Methane and carbon-dioxide percentage in gas were analyzed using a Shimadzu GC14-A gas chromatograph (Shimadzu Scientific Instruments, Columbia, MD) using a thermal conductivity detector (TCD). Helium was used as the carrier gas with 17 mL/min flow in the detector column. For measuring the ammonia stripping from the aerobic digesters, an annular denuder (URG Crop.) was used with internal coating of 1% citric acid solution. Annular denuder preparation and sampling was done as it is mentioned in Compendium of Methods for Inorganic Air Pollutant (Method IO-4.2)

Samples for VFA and anion analysis were collected twice a week. VFAs and dissolved anions (NO_2^-, and NO_3^-), samples were centrifuged at 10,000 g for 20 min at 25 ^oC followed by 1.5um filtration. The filtered samples were frozen and then thawed at room temperature for analysis. Thawed samples were centrifuged at 5,000 g for 10 min and filtered further at 0.45 µm. 900 µL VFA samples were acidified by adding 100 µL phosphoric acid and were analyzed using a Shimadzu GC-14-A gas chromatograph with a flame ionization detector. Helium, nitrogen, and hydrogen were the main gases used for analysis purpose. Air was used for makeup and flow rate of different gases were:

1. Helium – 17 mL/min
2. Nitrogen – 13 mL/min,
3. Hydrogen – 45 mL/min, and
4. Air – 450 mL/min.

Anion concentration in the samples were measured using Dionex D-120 ion chromatograph (Dionex Corp., Sunnyvale–CA). For cation measurement, CS-12 column equipped with conductivity detection with self generating suppression of eluent. 20mM methanesulfonic acid was used for eluent at 1 mL/min flow rate, while for anion measurement AS9-HC column was used with AG9-HC guard column.

Oxidation and reduction potential (ORP) in the aerobic digesters was measured using the OPR probe (Model 96-78-BN) from Thermo Electron Corp. and light solution was used to calibrate the instrument. Due to the volatile environment in the aerobic digesters ORP measurements were taken after 1 min after introducing the probe in the aerobic digester.

2.3 Results and Discussion

2.3.1 Anaerobic Digester performance

Phase-I **-** For the first phase of study, anaerobic detention times were selected to support the data for another study running in parallel. A six day aerobic SRT was selected for aerobic digestion of volatile solids to provide sufficient time for nitrifying bacteria to grow.

Phase-II **-** SRTs were selected in this phase to directly compare the performance of the thermophilic and mesophilic digestion and following aerobic digesters. Fifteen day anaerobic digestion was used since it is the most common detention time for anaerobic digestion. For aerobic digestion, 3 and 9 days SRTs were used to investigate in detail the effect of aerobic detention time on different performance parameters including VFAs, volatile solid reduction, and nitrogen removal from the anaerobic digested effluent. Table II-2 summarizes the average

values of parameters used for operation monitoring in digesters operated during Phase-I and Phase-II.

Data including low volatile solid reduction (Figure II-2), a high concentration of VFAs (Table II-3), and a small volume of gas production (Figure II-3), high TKN (Figure II-8) indicated that the second phase thermophilic digester (Th-15) performed poorly. The probable reason for poor performance of the digester was the change in the operations at Blue Plains. Blue Plains began sending very thick (7% solids) waste activated sludge and this was mixed and fed assuming that the concentration was only 4%.

The digester was maintained to evaluate the performance of the aerobic digesters for the case where the anaerobic digestion process functioned poorly. In the later phase of the study, the thermophilic digester performed better and data was collected for well functioning digester as well.

Table II-2 - Digester operation parameters comparison (Average values with standard deviation)

Digester details and acronym	**Operating Volume (L)**	**Average pH**	**Average VFA (mg/L as acetic acid)**	**Average alkalinity in digester effluent (mg/L as $CaCO_3$)**
Thermophilic anaerobic digestion at 15 day SRT (Th-15)	37.5	7.32	4749 ± 1635	2840 ± 72
Thermophilic anaerobic digestion at 20 day SRT (Th-20)	20	7.74	683 ± 384	7222 ± 518
Mesophilic Anaerobic digestion at 10 day SRT (Me-10)	15	7.34	73 ± 30	7191 ± 753
Mesophilic anaerobic digestion at 15 day SRT (Me-15)	37.5	7.34	276 ± 122	2833 ±155
Aerobic digester receiving influent from Th-15 with 3 day SRT (ThAer3)	3	7.32	357 ± 332	757 ± 32
Aerobic digester receiving influent from Th-20 with 6 day SRT (ThAer6)	4.2	6.75	103 ± 42	1340 ± 342
Aerobic digester receiving	6.3	7.18	147 ± 73	576 ± 323

influent from Th-15 with 9 day SRT (ThAer9)				
Aerobic digester receiving influent from Me-15 with 3 day SRT (MeAer3)	3	6.98	123 ± 83	337 ± 67
Aerobic digester receiving influent from Th-10 with 6 day SRT (MeAer6)	6	7.03	55 ± 16	1449 ± 335
Aerobic digester receiving influent from Me-15 with 9 day SRT (MeAer9)	6.3	6.49	50 ± 26	277 ± 29

The large variation in the alkalinity and pH in aerobic digesters was due to variations in the feed composition, nitrification and denitrification. The nitrification process consumes alkalinity and along with the loss in alkalinity, the pH also dropped during aerobic digestion.

VFAs were measured in the digester liquid to monitor anaerobic digester performance and data are summarized in Table II-3. Higher total VFA concentration, but with lower acetic acid concentrations were observed in thermophilic digesters in comparison to the mesophilic digesters. Additionally, the data also show that more than 50% VFA were removed from the anaerobic effluent during the aerobic digestion. During the anaerobic digestion upset period the thermophilic digester (Th-15) produced comparatively more VFA, but the aerobic digesters were able to remove more than 94% of the VFA at minimum 3 day SRT.

Table II-3 – Distribution of major volatile fatty acid (VFA) concentrations in different sludges and comparison of different VFA fractions with total VFA concentration.

Sludge		Acetic Acid (C2)	Propionic Acid (C3)	Iso-butyric & Butyric Acid (C4)	Total VFA
		(mg/L)			(mg/L as acetic acid)
Th-15		862	1,097	1,593	5,988
Th-20		240	190	49	683
Me-10		54	8	6	73
Me-15		160	194	53	277
ThAer3		235	53	50	357
ThAer6		60	17	14	103
ThAer9		109	20	24	147

MeAer3		91	15	21	123
MeAer6		36	3	11	55
MeAer9		33	1	11	50

2.3.2 Volatile solids removal during anaerobic and aerobic digestion

Volatile solid removal in anaerobic digestion **-** Measurements of total solid and volatile solid were conducted for all digesters over the period of operation. Inman et al (2004) investigated the effect of temperature and SRT on anaerobic digestion and VS reduction for Blue Plains sludge. Their study showed that Blue Plains sludge has a higher VS reduction during mesophilic digestion than thermophilic digestion. The results from this study also show similar results, data in Figure II-2 provide a comparison of the VS removal during anaerobic digestion at different SRTs and temperatures. Volatile solids removal in thermophilic digester operating at 20 day SRT is equivalent to the VS removal in the mesophilic digester operating at 15 day SRT.

COD removal and gas production **-** The thermophilic digester operating at 20 day SRT yielded the highest volume of gas among all four anaerobic digesters operated during the study. Gas yield from Th-15 was lower than reported by Inman (2004) due to the poor performance of this digester. Figure II-3 show that irrespective of SRT differences in Phase-I and Phase-II, the anaerobic digesters during Phase-I produced more gas and more methane compared to the anaerobic digesters in Phase-II. In Figure II-3, the gas production data for the thermophilic digester (Th-15) was from the later part of Phase-II when the digester had recovered to a more normal operation.

COD measurements from different sludges and data suggest that more than 70 % total COD removal can be achieved using the mesophilic-aerobic digestion sequence. The thermophilic-aerobic digestion sequence could be expected to attain more COD removal, but from this study no concrete statement can be made because the Th-15 digester performed poorly. Figure II-4 show that COD removal for the combination of Th-20 anaerobic followed by 6 days aerobic digestion was the highest (80%). Figure II-4 also shows the COD removal for the aerobic stages. The data show that the aerobic stage at 3 day SRT can remove an additional 40% – 45% COD.

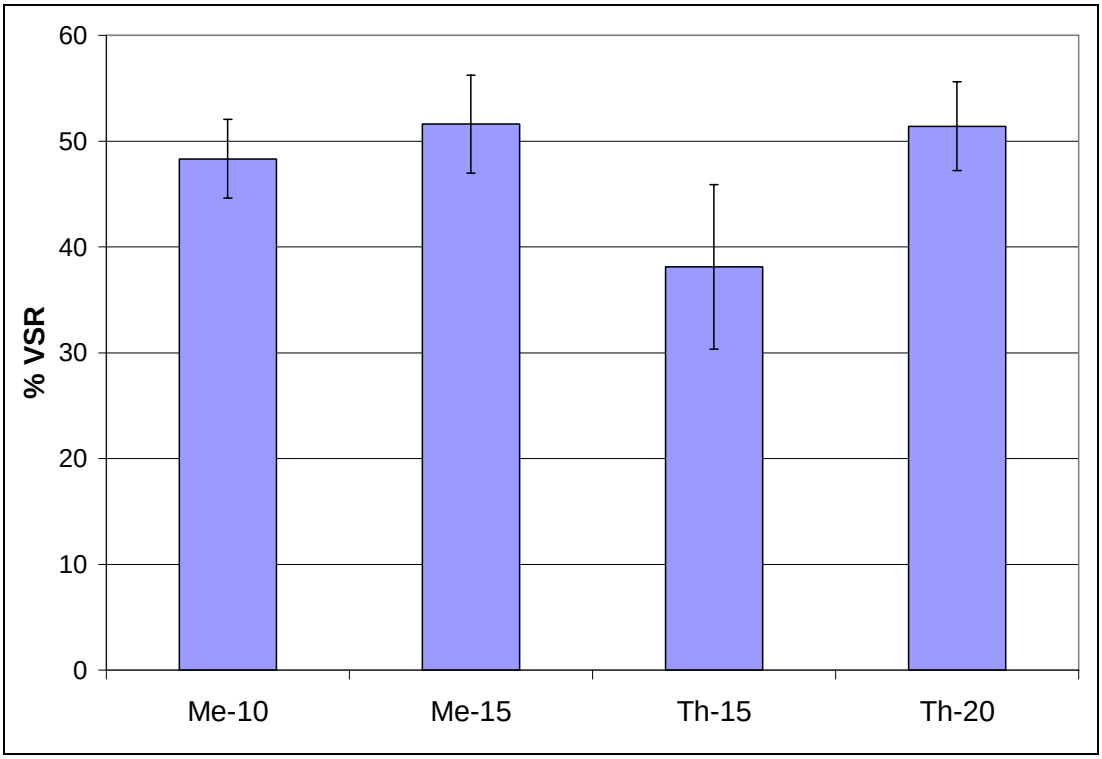

Figure II-2 – Comparison of volatile solids reduction in different anaerobic digesters operation at different SRTs. Th-15 VSR data is from digester recovery period.

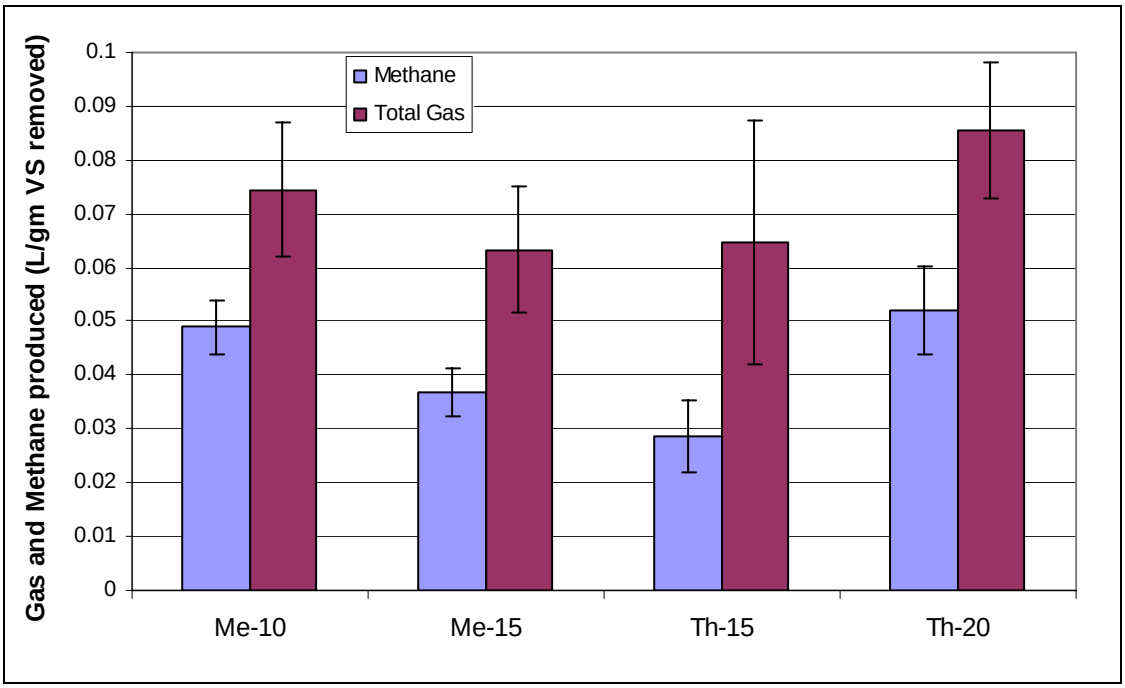

Figure II-3 – Comparison of methane production in different anaerobic digesters vs total gas produced per day

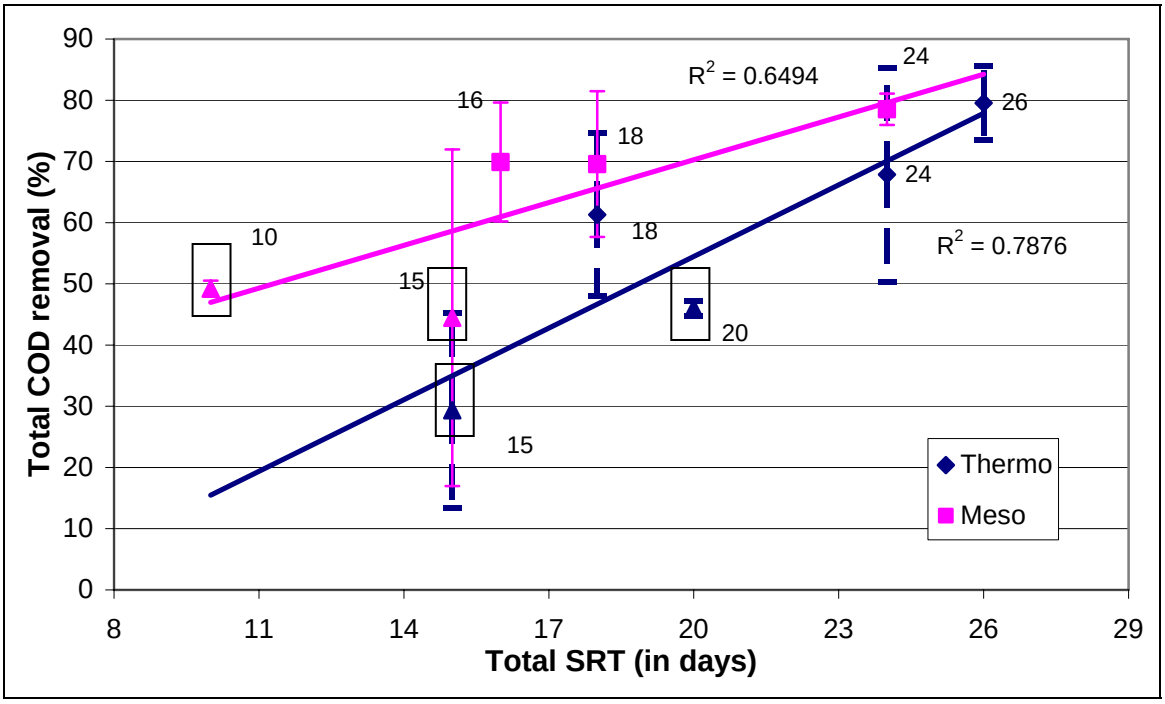

Figure II-4 – Comparison of COD removal from anaerobically digested effluent in aerobic digestion stage. COD removal increases with increase in the SRT and influent temperature. Data from anaerobic digesters are boxed to mark additional COD removal during aerobic digestion and the total digestion SRTs are marked along.

Effect of aerobic digestion SRT on VS reduction -

Work by Novak and Higgins (1997) and Novak and Murthy (2001) suggested that there are two different types of biopolymers, which are degraded during aerobic and anaerobic digestion. Park et al. (2003) conducted batch studies for aerobic-anaerobic sequential digestion and anaerobic-aerobic sequential digestion. The results suggested that overall VS reduction resulting from the both sequences is the same (approximately 60%), the only difference being the ratio of VS reduced under anaerobic digestion process and aerobic digestion. Their research results also suggest that some portion of the volatile solids cannot be degraded by either of these digestion processes and some portion can be degraded by both anaerobic and aerobic digestion processes.

In this study, the effect of the aerobic digestion SRT on total volatile solids removal was investigated. Three different aerobic digesters were operated at different SRTs receiving anaerobically digested sludge as the feed. Figure II-5 compare the VS reduction at different

SRTs and suggest that more than 60% volatile reduction can be achieved with an aerobic SRT as low as 3 day, with the exception of digester ThAer3. The data also show that when the aerobic phase SRT is increased, the total VS removal increases. Comparison of volatile solids removed during the aerobic digestion from the anaerobic sludge (thermophilic and mesophilic) is in accordance with the finding from work done by Novak and Higgins (1997), Novak and Murthy (2001) and Novak and Park (2003) and supports the presence of an independent organic fraction which is removed only by the aerobic digestion processes. Aerobic digestion SRT with a 3 day SRT can remove additional 20% or more volatile solid during the aerobic digestion , and increase in aerobic digestion SRT increases the percentage of volatile solids removal (Figure II-6).

Effect of aerobic digestion on poorly digested sludge - During the second stage of this investigation, the thermophilic digester failed to perform as expected and this resulted in a low volatile solids reduction. The average VS reduction measured during this period of operation was 16.5% (± 7.75%). Upon subsequent aerobic digestion of poorly digested biosolids from the thermophilic digester, approximately 40% total VSR was achieved at a 3 day aerobic SRT.

A comparison between the volatile solids removal during the poor performance and good performance of thermophilic anaerobic digestion is shown in Figure II-7. The data show that aerobic digestion has positive effect on VSR, especially when the anaerobic stage performs poorly. During the poor anaerobic digester performance, more than 20% additional VS removal was achieved by aerobic digestion at a detention time of 3 days, compared to 14% when the anaerobic digester was performing properly.

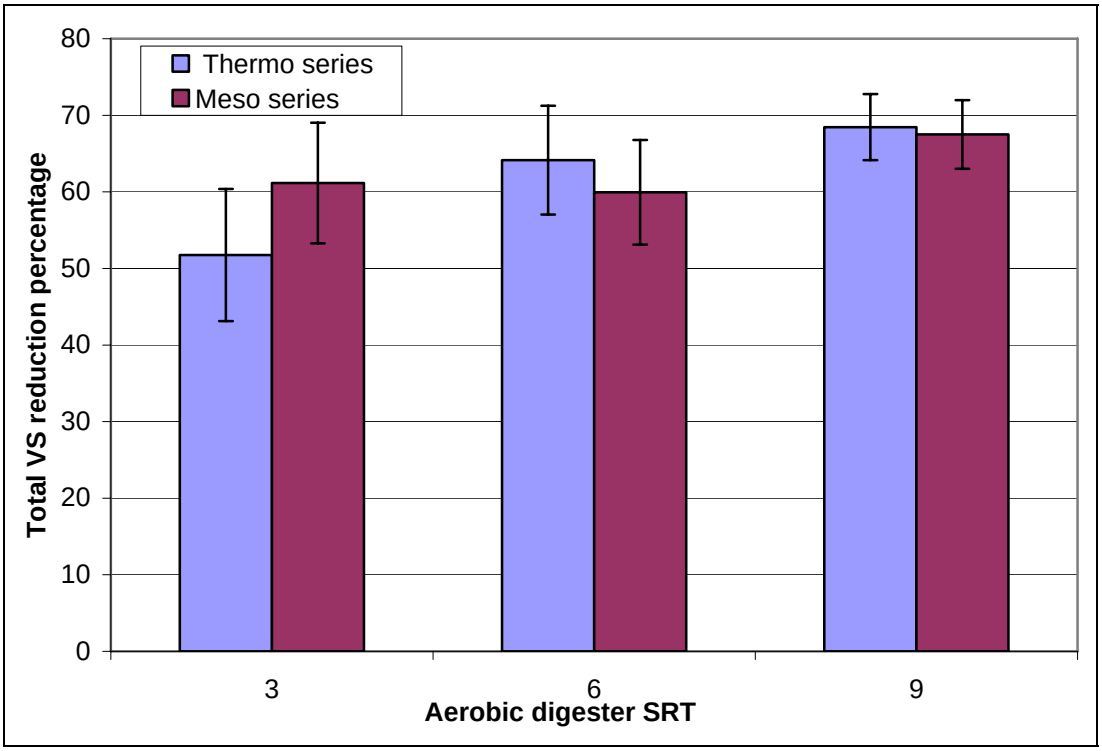

Figure II-5 – Comparison of aerobic phase digestion SRT and effect of anaerobic digestion process on volatile solids removal.

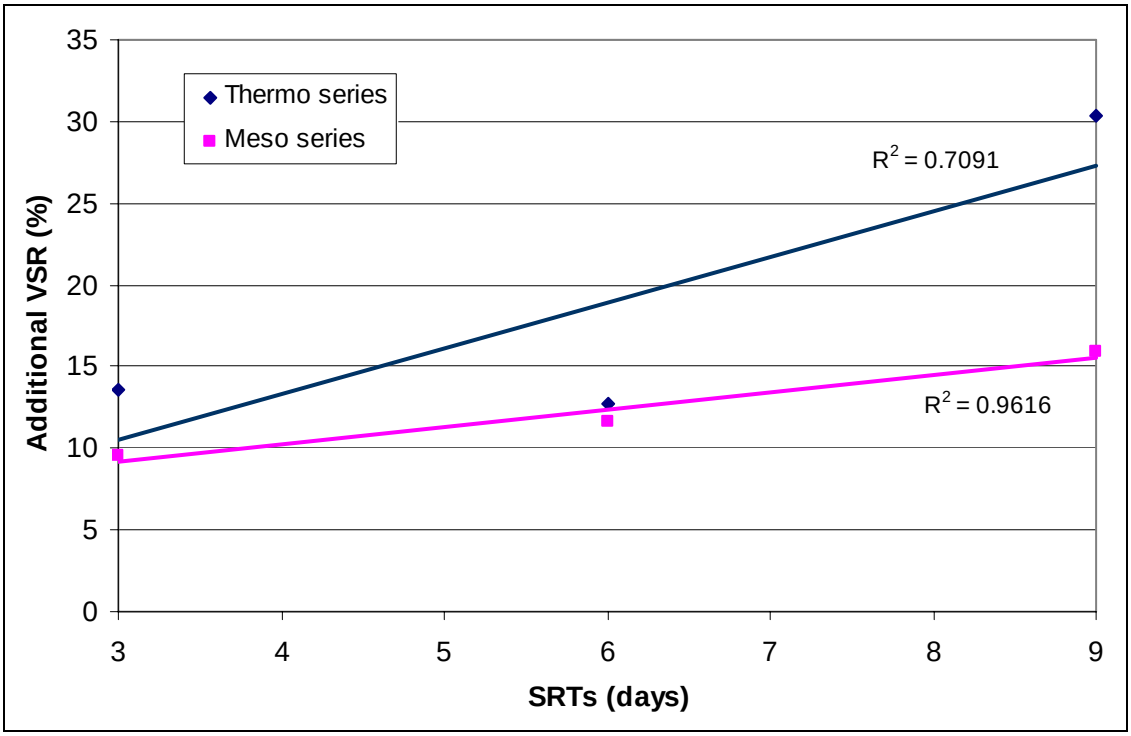

Figure II-6 – Comparison of VS removal from different influent during aerobic digestion process. Solid lines represent the linear fitting of data.

Previous work (Novak and Murthy, 2001 and Novak and Park, 2004) and this study (Figure II-6 and Figure II-7) suggest that there exist four significant fractions of volatile solids that can be degraded under –

1. Aerobic conditions (type-1),
2. Anaerobic conditions (type-2),
3. Both Aerobic and anaerobic conditions (type-3), and
4. Neither under aerobic nor anaerobic conditions (type-4).

During the normal operation of sequential anaerobic-aerobic digestion, the anaerobic stage digester removes the type-2 fraction and major portion of type-3 VS fraction. In the following aerobic digester the type-1 fraction and some additional portion of type-3 VS fraction get removed.

The anaerobic digestion upset study suggests that, when anaerobic digestion gets upset, only a small portion of type-2 and type-3 VS fractions is removed during the anaerobic stage. It is the later aerobic stage which removes the major portions of VS fractions of type-1 and type-3, saving the overall digestion process from failure. The Figure II-7 shows that minimum 3 day of aerobic digestion helped to achieve upto 40% VSR even with a poorly performing anaerobic digester.

Anaerobic-aerobic sequential digestion also has an engineering advantage. It may provide the option of optimizing the SRT of the anaerobic and aerobic phases (Figure II-7) for minimizing the cost and energy requirements for the operation. Optimized anaerobic-phase and aerobic phase SRTs may simultaneously remove higher volatile solids with less digester volume and a low energy consumption.

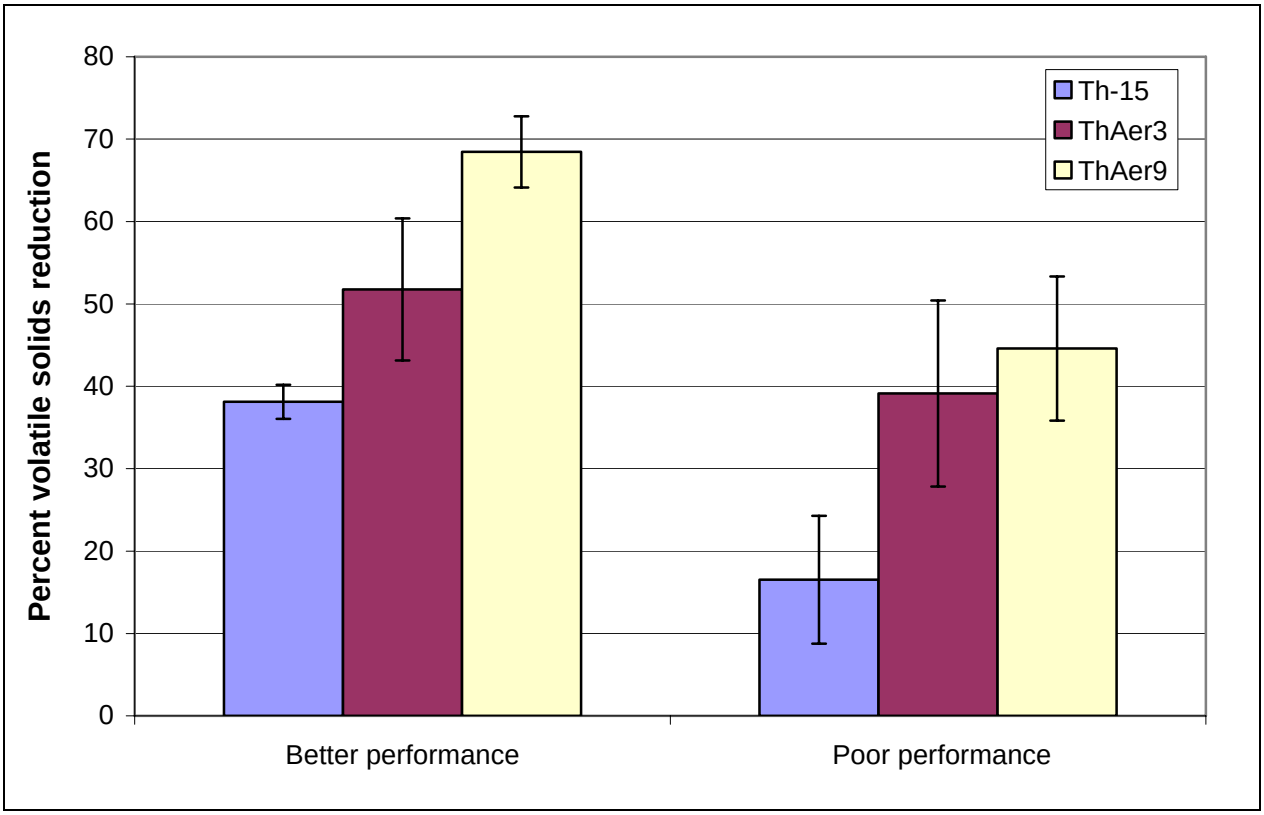

Figure II-7 – Comparison of performance of thermophilic digestion on VSR and role of aerobic digestion in attaining cut-off VSR limits.

2.3.3 Nitrogen removal

Nitrogen removal in sequential anaerobic-aerobic digestion **-** Anaerobic digestion releases protein which is bound in the floc and upon protein degradation a high concentration of ammonia is produced. When the digested sludge is dewatered, the water that is removed is recycled back into the wastewater treatment plant. This process adds a higher nitrogen and carbon load to the plant. Akunna et al (1994) have shown more than 95% carbon and 70% ammonia-nitrogen removal from anaerobic-aerobic sequential filters for wastewater treatment. It was expected in this study that a similar nitrogen removal performance could be achieved with no external source of carbon. The carbon source for denitrification was expected to come from the soluble organic matter present in the anaerobically digested sludge, which include volatile fatty acids, polysaccharides and protein and the solid fraction of VS degraded by aerobic digestion. During both phases of study, TKN and ammonia in both the anaerobic and aerobic digesters were measured. Figure II-8 show that up to 1,200 mg-N/L TKN and 500 mg-N/L ammonia is present

in the anaerobic digesters with the exception of Th-15 anaerobic digester (which had both TKN and ammonia higher than other anaerobic digesters). During the aerobic digestion both TKN and ammonia were found to decrease (Figure II-9 and Figure II-10).

After six days aerobic digestion both ammonia and TKN are higher than the corresponding level at 3 days and 9 days of digestion. This difference may be due to the change in the feed characteristics shipped from Blue Plains. Table II-3 details the nitrogen mass balance during aerobic digestion and it suggests that more than 50% of the influent total-nitrogen is lost. Quantification of the loss of ammonia and TKN presented in Figure II-10 shows that 3 days of aerobic digestion can attain more than 60 % TKN removal and 75% ammonia removal from the liquid phase. Figure II-9 and Figure II-10 also suggest that more nitrogen can be removed from the thermophilic digested influent after 6 days than mesophilic digested influent. Higher removal from the aerobic digesters (Thermo series) receiving the thermophilic digested influent may be due to the higher concentrations of readily available VFAs which are a preferred carbon source for denitrification (Akunna et al, 1993).

Table II-4 - Nitrogen Mass balance in aerobic digesters (All masses are in mg-N/day). Nitrate and nitrite in the anaerobic influent digester were lower than the measurable concentration.

Digester	**ThAer3**			**ThAer6**			**ThAer9**	
	In	Out		In	Out		In	Out
TKN	1,530	743		1,003	350		1,071	443
NO_2	NA	0		NA	9		NA	0
NO_3	NA	1		NA	1		NA	2
NH_3(gas)	NA	13		NA	23		NA	26
Total	1,530	757		1,003	383		1,701	470
Loss %		50.6			61.9			56.1
Digester	**MeAer3**			**MeAer6**			**MeAer9**	
	In	Out		In	Out		In	Out
TKN	1,147	502		1,324	650		802	280
NO_2	NA	38		NA	2		NA	0
NO_3	NA	2		NA	0		NA	12
NH_3(gas)	NA	15		NA	31		NA	33
Total	1,147	558		1,324	684		802	326
Loss %		51.3			48.4			59.5

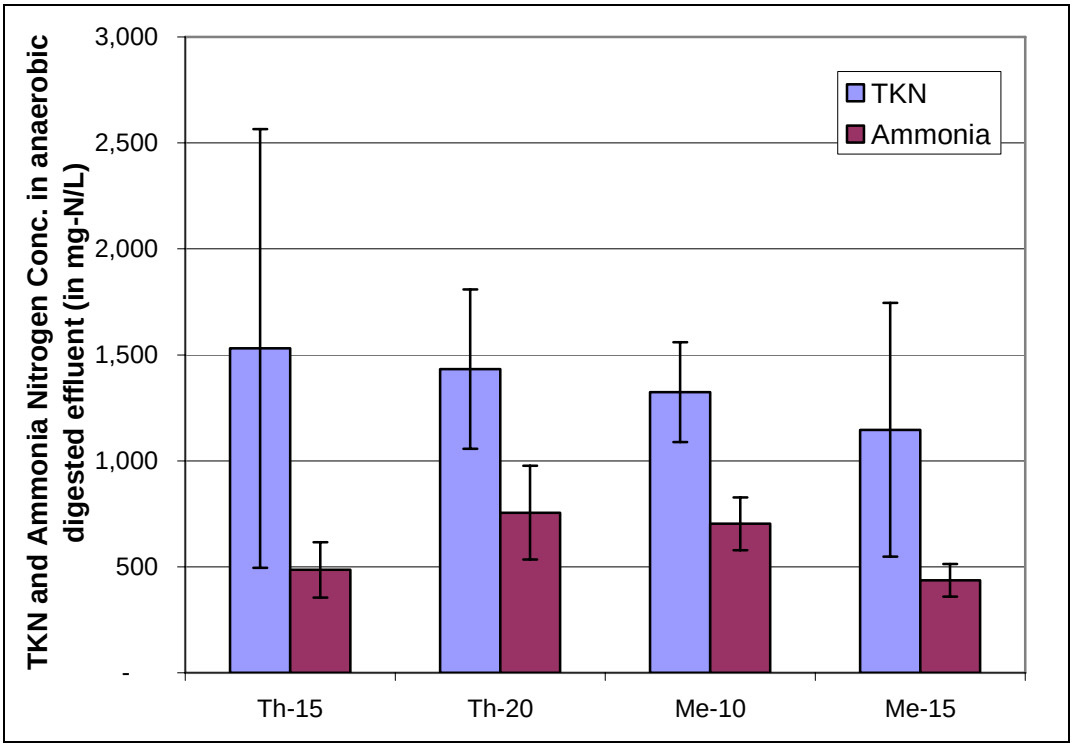

Figure II-8 – Effect of temperature and anaerobic phase digestion period on the release of NH_3 due to degradation of proteins. Comparative TKN, organic nitrogen content and ammonia levels in different digesters are presented as well.

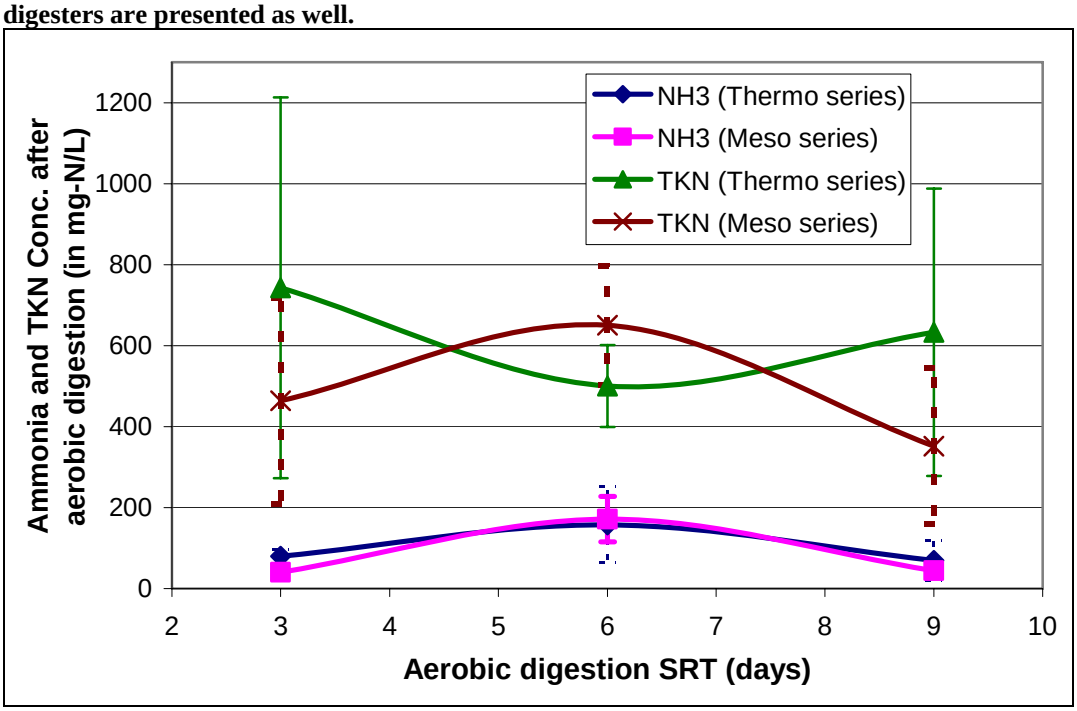

Figure II-9 – Typical TKN and ammonia concentration in aerobic digested effluent operated at 3, 6 and 9 day.

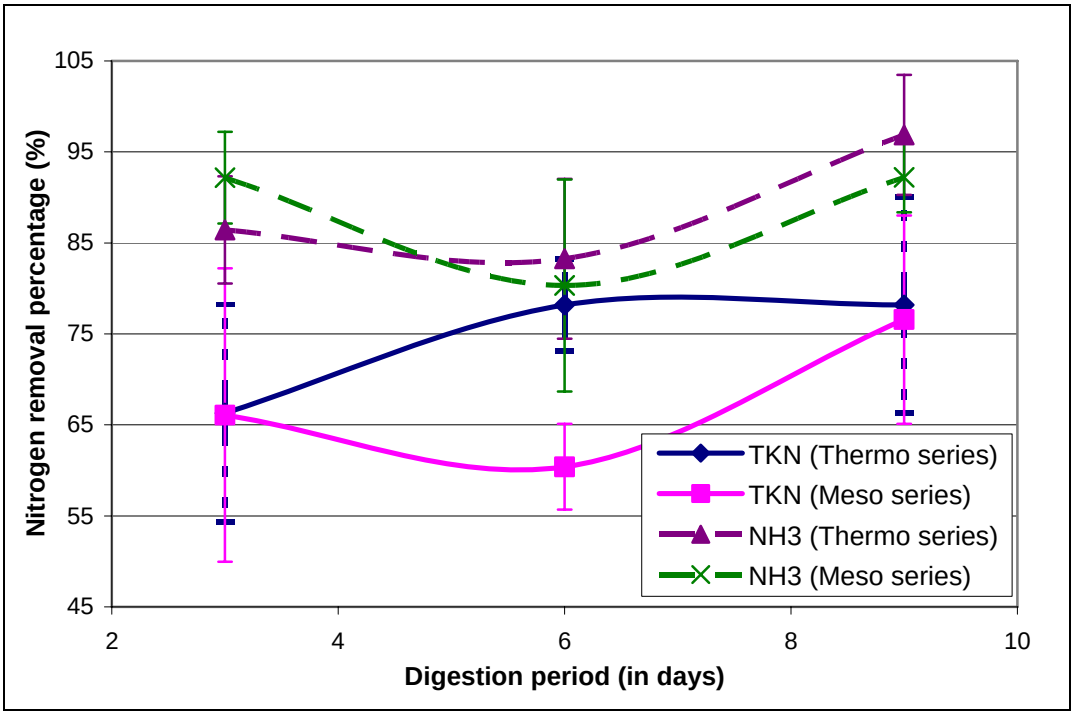

Figure II-10 – Effect of aerobic phase digestion period and influent characteristics on the nitrogen removal in aerobic digestion phase (on mg-N/L basis). Figure shows percentage of TKN and NH_3 removed with digestion period in aerobic digesters.

For investigation of nitrogen loss during aerobic digestion, nitrate and nitrite were measured. It was observed (Figure II-11) that at smaller SRT higher concentrations of nitrite were present, but at longer SRTs higher concentrations of nitrate were present. It was thought that denitrification accounted for the nitrogen removal due to the low nitrate and nitrite levels in the aerobic effluent. Following the nitrification experiments, investigations were carried out to determine if nitrogen loss were due to ammonia stripping or denitrification.

Stripped ammonia gas was captured using a denuder (URG corp.) with 1% citric acid solution. It was found that ammonia stripping accounts for only for less than 10% (with exception of 11% in MeAer9 digesters) nitrogen loss during the aerobic digestion (Table II-4). For measuring the denitrification potential, the ORP profile in the aerobic digesters was quantified as indicated in Figure II-12 and Figure II-13. The data show that in all aerobic digesters when sludge was added, reducing conditions occur and support the denitrification. Work done by Helmer and Kunst

(1998) and Bernet et al (2000) also supports the possibility of simultaneous nitrification and denitrification using the nitrite and nitrate as the electron acceptor.

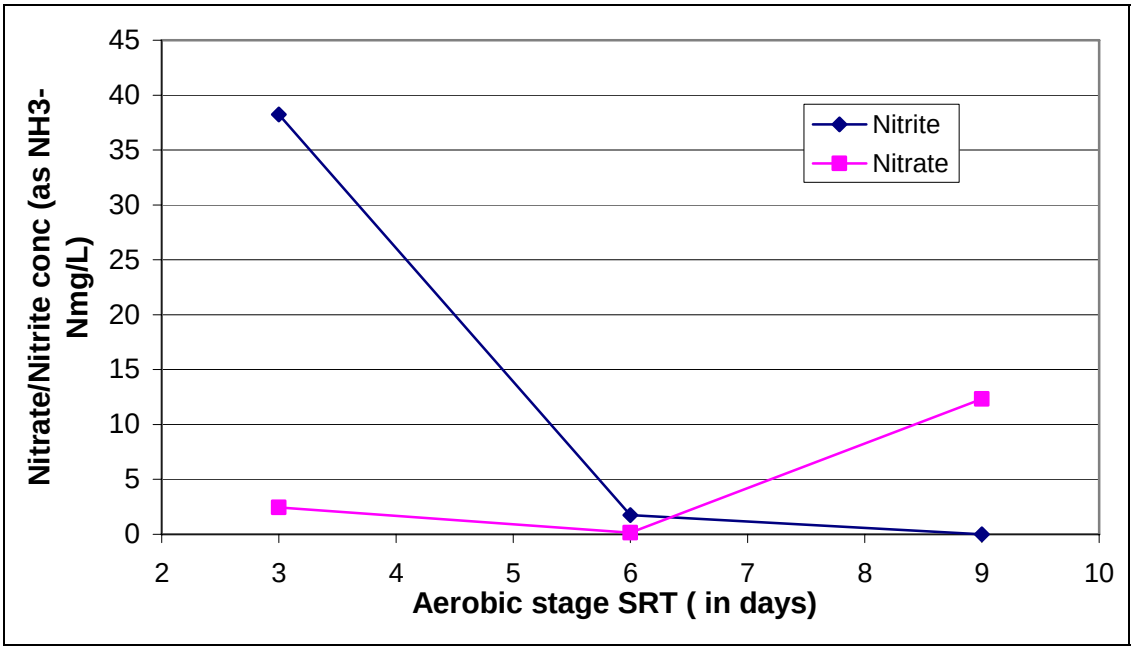

Figure II-11 – Effect of aerobic stage SRT on the residual Nitrate and Nitirite concentration in the aerobic digested effluent.

A study by Akunna et al (1993) suggested that VFA and glucose are the preferred carbon sources for the denitrification. Their study suggested that the amount of residual carbon source is one of the limiting criteria in denitrification process. During this study, it was found that more COD and VFA were present in the thermophilic anaerobic effluent in comparison to that in the mesophilic anaerobic effluent and it is believed that the higher concentration of VFAs in thermophilic digester effluent is responsible for higher nitrogen removal (Figure II-9 and Figure II-10).

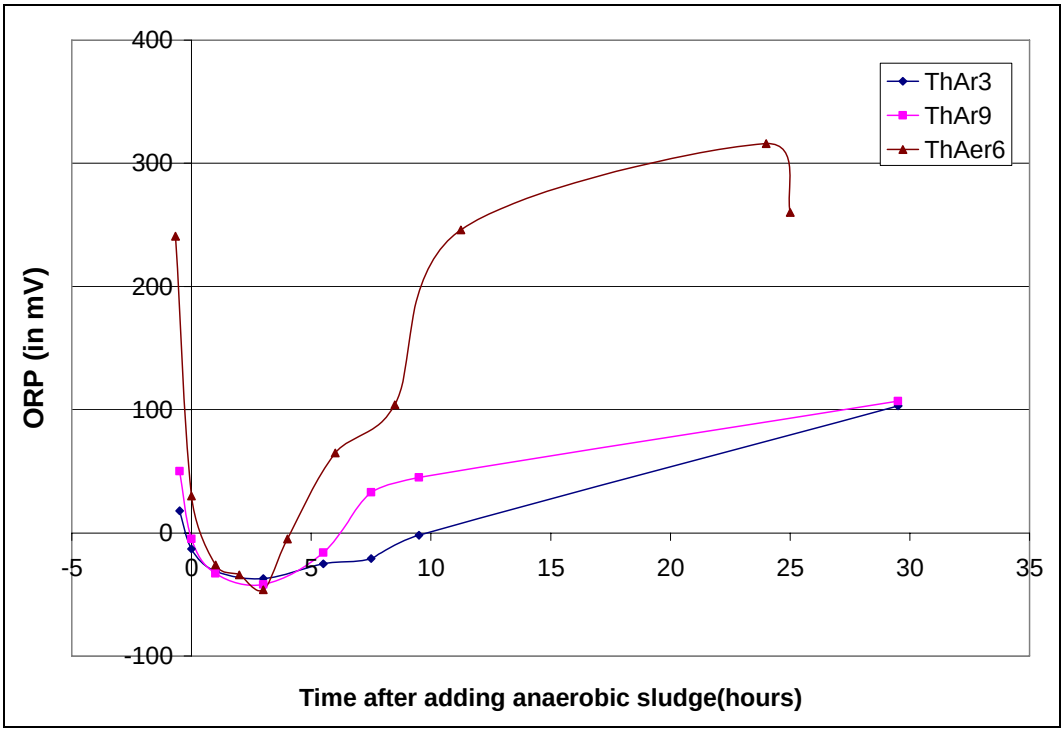

Figure II-12 – ORP profile for the aerobic digesters operated at 3, 6 and 9 day SRT receiving thermophilic influent. Anaerobic condition with reducing environment exists for 10 hrs after addition of anaerobic digested sludge. ORP adjusted to represent potential with respect to H_2/H^+ cell.

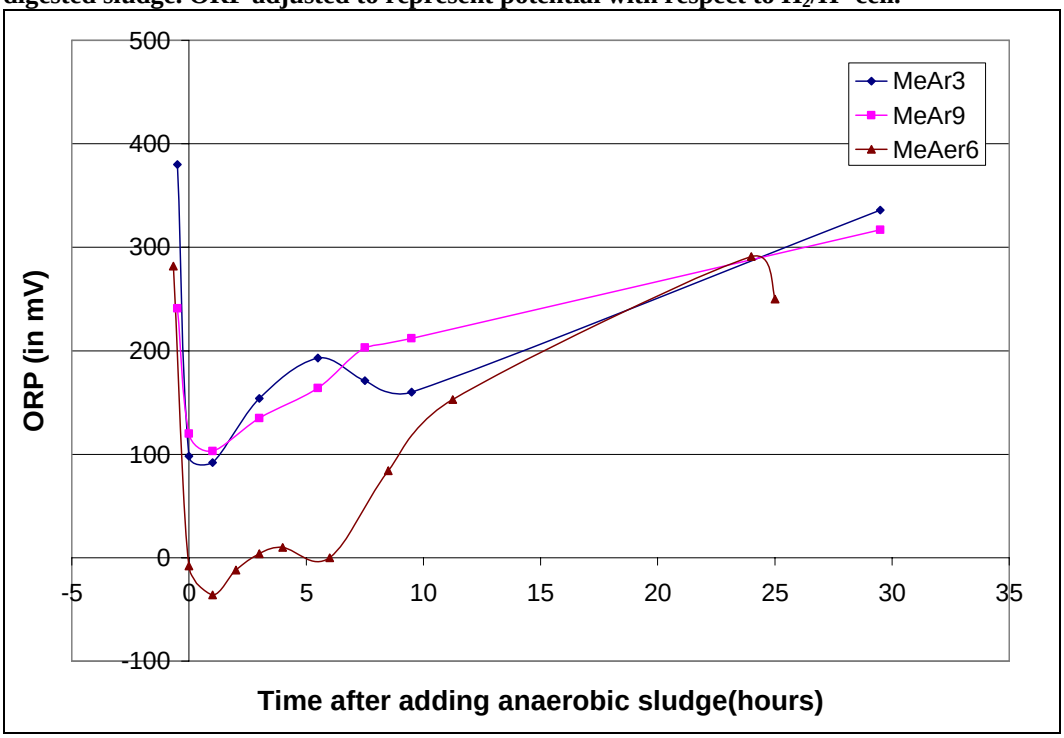

Figure II-13 – ORP profile in aerobic digesters receiving mesophilic digested influent. ORP adjusted to represent potential with respect to H_2/H^+ cell.

2.4 Summary and Conclusions

The analysis of results obtained from the study suggests that the anaerobic-aerobic digestion sequence provides several advantages over single-phase and two-phase anaerobic digestion processes. Sequential anaerobic-aerobic digestion help in achieving higher volatile solids removal, nitrogen removal and aerobic digester safeguard the whole digestion process when anaerobic digestion process gets upset. The main nitrogen removal mechanism in aerobic digesters appears to be simultaneous nitrification and de-nitrification process, as evidenced by the absence of significant concentration of NO_2^-/NO_3^- and the existence of anaerobic conditions for certain duration after feeding the aerobic digesters with anaerobic sludge. Additional studies are required to confirm the simultaneous nitrification/denitrification process in the sequential digestion process.

The advantages of the anaerobic-aerobic digestion process can be summarized as -

1. Up to 60 to 70% COD removal can be obtained with minimum 3 day aerobic digestion in the sequential anaerobic-aerobic digestion.
2. High volatile solid reduction can be achieved during sequential digestion process even if anaerobic digestion process is not functioning properly. A 3 day aerobic digestion time was able to achieve more than 40% overall VS reduction when the thermophilic anaerobic digester was performing poorly.
3. An additional 10% to 20% VSR can be achieved during aerobic digestion of anaerobically digested sudge. Thermophilically digested sludge showed a higher extra VS removal during the aerobic stage in comparison to mesophilically digested sludge.
4. Increasing the aerobic digestion period from 3 to 9 days increases the TKN and ammonia removal from the system. A minimum 80% ammonia removal and more than 50% TKN removal was measured during this study.
5. TKN and ammonia removal by anaerobic/aerobic is better in thermophilically digested solids, than with mesophilically digested solids, with thr exception of 3 day aerobic digestion period.

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Chapter 3

Sequential Anaerobic-aerobic digestion for Odor reduction and improvement in dewatering properties of digested sludge

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Abstract

Sequential anaerobic-aerobic treatment is a well established technology for wastewater treatment, but its use for sludge digestion has received less attention. In this research, protein and polysaccharide concentrations in anaerobic and followed by sequential aerobic digesters were monitored. More than 30 % and up to 85% of the combined protein and polysaccharides present in the anaerobic digester were degraded after sequential anaerobic-aerobic digestion. Improvement in the dewatering properties was also found as evidenced by the decrease in CST and the polymer dose requirement for the sequentially digested sludge. Following sequential anaerobic–aerobic digestion, it was found that sludges that were digested under thermophilic anaerobic conditions produced approximately 30% lower odors than mesophilic digested biosolids and the addition of an aerobic digestion step reduced odors an additional 40%. Freeze-thaw treatment of digested biosolids showed that even after anaerobic-aerobic digestion, sludges retain a potential for high and rapid odor production. It appears that following freeze-thaw treatment, additional proteins are made bioavailable, resulting in the higher odor generation.

Keywords: Dewatering, Biosolids, Odor, Freeze thaw, Anaerobic aerobic digestion, thermophilic digestion and mesophilic digestion.

3.1 Introduction

Anaerobically digested sludges are often found to have poor dewatering properties and may also generate odors, especially if the dewatering process includes high solids centrifugation. Poor

dewatering and strong odors are the cause of concern for wastewater treatment utilities due to the additional costs for conditioning polymers and public relations problems associated with odors.

The release of biopolymers, primarily proteins and polysaccharides, into solution during digestion is considered to be responsible for deterioration of dewatering properties (Novak et al, 2003). Research by Novak and Higgins (1997) and Novak and Murthy (2001) suggest that there are two different types of biopolymer which are released during anaerobic and aerobic digestion. During aerobic digestion, polysaccharides accumulate due to the low activity of polysaccharide degrading enzymes. In anaerobic digestion, protein accumulates in solution and the ratio of protein to polysaccharides is found to be higher than that in aerobic digestion. Frølund et al (1996) proposed that activated sludge consists of a matrix of micro-organism and biopolymers, bound by cations. In the sludge matrix, the approximate content of biopolymer is – proteins 50%, polysaccharide 20%, DNA 1% and humic materials 20%. Novak and Higgins (1997) have found that some polysaccharides are bound with lectin-type proteins present in sludge floc by Calcium (Ca) and Magnesium (Mg). Other investigations by Murthy et al (2000) and Muller et al (2001) suggests that proteins present in sludge have a strong tendency to bind with trivalent cations. Cations, including Ca, Mg, Iron (Fe) and Aluminum (Al) were found to be a critical component of the activated sludge floc structure and thus play an important role in sludge digestion processes, dewatering and odor generation. Investigations into the role of aluminum in sludge floc are relatively few compared to iron. It is thought that aluminum selectivity for polysaccharide and humics is higher than iron, while iron more favorably binds to proteins (Lu, et al, 1999). Novak and Muller (2001) found that among the different oxidations states of iron, Fe (III) binds solution protein more efficiently than Fe(II).

Recent studies at Virginia Tech., have shown that cations play an important role in floc destruction during anaerobic and aerobic digestion. Park et al (2005) found that the total VS reduction by either anaerobic-aerobic digestion or aerobic-anaerobic digestion is the same; only portions of VS removed during the separate anaerobic or aerobic stage changes. This suggests that there is some portion of VS that can be degraded only during aerobic digestion and some

portion degraded only under anaerobic conditions. In the same study of different sludges, Park et al (2005) found that protein release during anaerobic digestion was strongly correlated with VS removal. The iron concentration in the feed sludge to an anaerobic digester could be correlated to the percent VS reduction, while an increase in calcium and magnesium in solution was associated with increased solids destruction by aerobic digestion. Subramanian (2005) found improved dewatering for sequential anaerobic-aerobic digested biosolids due to the reduction of bound water and low concentration of proteins and polysaccharide.

Verma (2005) in a study of 11 treatment plant's sludges found the role of metals is important in odor generation from the biosolids. Their study suggests that the peak organic sulfur decreases with an increase in the digestion period of the sludge, but VS reduction showed a poor correlation with sulfur odors. It was suggested that the iron content in the digested sludge is the main constituent that controls organic sulfur gas generation. Higgins et al (2006) suggested that methanogens play an important role in controlling the odors by consuming the organic-sulfur gases.

The literature suggests that both anaerobic and aerobic digestion processes degrade significantly different portions of sludge but a fraction of solids can be digested under both digestion processes. Therefore, by utilizing combined anaerobic-aerobic digestion, higher solids destruction and lower odors generation might be possible. The major objective of this study was to determine the effect of sequential anaerobic-aerobic digestion on odor production and to understand the effects of freeze thaw conditions on the odor production potential of digested sludges. Another objective of the study was to investigate the dewatering properties of sequentially digested sludges.

3.2 Material and methods

3.2.1 Bioreactor operation:

The study was divided into two phases and during both phases, two anaerobic digesters, one thermophilic (55 ^{o}C) and another mesophilic (35 ^{o}C) were used for the first stage anaerobic

digestion. Aerobic digestion at 30 ^{o}C followed anaerobic digestion. All of the digesters were housed in a constant temperature room for maintaining the desired temperatures. Table III-1 shows the SRTs of the different anaerobic-aerobic digester combinations studied during the different phases and also provides the nomenclature that is used in the discussion and analysis of the results for the digesters.

Table III-1 - Digester combination during two phases of study and acronyms of the digesters used during result analysis

Study phase	**Combination – 1 (SRTs)**		**Combination – 2 (SRTs)**	
	Thermophilic anaerobic digestion (55 C) - Stage 1	**Sequential Aerobic digestion (30 C) - Stage 2**	**Mesophilic anaerobic digestion (35 C) - Stage 1**	**Aerobic digestion (30 C) - Stage 2**
I	20 days (Th20)	6 days (ThAr6)	10 days (Me10)	6 days (MeAr6)
II	15 days (Th15)	9 days (ThAr9)	15 days (Me15)	9 days (MeAr9)
		3 days (ThAr3)		3 days (MeAr3)

Anaerobic digesters were fed with feed prepared from gravity thickened primary sludge and dissolved air flotation (DAFT) waste activated sludge in a 1:1 ratio (by weight). The feed solids percentage was maintained 4%. Both primary and secondary sludge was provided from the Blue Plains wastewater treatment plant operated by the District of Columbia Water and Sewer Authority (DCWASA) on weekly basis by overnight shipment. The sludge was stored at 4 ^{o}C until used. Feed was provided once per day and an equivalent volume of digested sludge was taken out from the digester. The anaerobic effluent was fed to the aerobic digester to keep the SRT constant.

For anaerobic digestion, plastic conical (egg-shaped) fermenters manufactured by Hobby Beverage Equipment Company were used. Anaerobic digesters were mixed by re-circulating gas from the headspace to the bottom of digester using a Cole-Parmer 6-600 RPM variable speed pump. No extra heating was provided for maintaining the temperature of the mesophilic

digesters, but for thermophilic digesters, hot water at 63 ^{o}C was re-circulated through poly-vinyl tubes along the periphery of thermophilic digester and the entire system was wrapped up in insulating material to avoid heat loss. Gas produced during anaerobic digestion was collected in 30 liter air tight Tedlar gas bags (Fisher Scientific) and periodic measured for the gas volume and gas content. Due to the higher operating temperature, water evaporated from the thermophilic digester and it was captured using water trap. The average water loss was 50 ml per day and this water was reintroduced in the digester on a periodic basis.

Aerobic digestion was carried out in stainless steel digesters provided by Blinchmann Engineering, except for three day aerobic digestion. For the three day aerobic digestion, 9 L glass digesters (Fisher Scientific) were used due to the low operation volume (only 3 L). For aerobic digestion, mixing was achieved using external pumps (Cole Parmer, 6-600 RPM) and air was supplied from a compressor and an aeration-stone was used to distribute the air. Due to the higher operation temperature and limitations in closing the digesters, water was lost due to evaporation. Water was reintroduced back in the system to the original volume every day by adding distilled water prior to sampling and wasting the effluent from the digesters. The dissolved oxygen level in all of the digesters was maintained at 3.0 ppm using flow regulation.

3.2.2 Analytical Methods:

For investigating dewatering properties, protein, polysaccharide, cations (including $NH4^{+}$, Na^{+}, K^{+}, Mg^{2+} and Ca^{2+}), capillary suction time (CST) and polymer dose consumption were measured periodically, while for odor generation, methods developed by Novak et al. (2002) and Muller et al. (2004) were used.

Biopolymer Analysis – Samples from the raw feed, anaerobically digested sludge and from the aerobic digesters were collected twice per week and centrifuged at 10,000 g for 20 min. The supernatant, filtered through 1.5 µm filters (934-AH, Whatman) was used for biopolymer and cation measurements. Samples were filtered and stored at 0^{o}C until used. Filtration using 0.45 µm nitrocellulose filters (Fischer Scientific) was done after frozen samples were thawed at room temperature, prior to cations measurement. Measurement of soluble proteins was done by the

modified Lowry et al (1951) method described by Frølund et al (1996). Soluble polysaccharides were measured by the Dubois et al (1956) method utilizing hexose as the standard.

CST and polymer dose quantification – A 1% (by weight) solution of solid polyacrylamide polymer, Stockhausen–650, was used for optimum polymer dose determination. For CST measurements, 100 mL of digested sludge conditioned with polymer and sheared using a Waring blender for 30 sec was used. Both a Triton Type 304-M and Triton Type 165 CST apparatus were used with Whatman 17-CHR chromatography paper. The optimum polymer dose was determined as the polymer dose providing the lowest CST.

Odor sample preparation and measurement – Odor samples were prepared by simulating the dewatering process of a high-solids centrifuge. At the optimum polymer dose, the sludge samples were sheared for 30 sec using a Waring blender. The resultant biosolids were dewatered in two steps, first by centrifugation in a lab centrifuge (operated at 10,000 g for 20 min at 25 C), followed by dewatering using hydraulic piston press by applying 30 psi pressure for 15 min with Whatmann 41 type filter paper as the filtering media. Five microliter of a 0.127 mM bromoethane sulfonic acid (BESA) solution was added before centrifugation to inhibit methanogenic activity for some of the sludge cakes. The biosolid cakes were incubated in 250 mL I-CHEM glass bottles, and sealed with caps fitted with a Teflon septa, at 25 C. Freeze-thaw samples were stored at 0 C for the desired period of freezing (1 week and 1 month) and thawed for 1 day at 25 C prior to odor testing. After thawing, the samples were dewatered using the lab centrifuge dewatering simulation procedure.

Odor measurements included quantification of H_2S (Hydrogen sulfide), CH_3S (methyl-thiol, MT), CH_3-S-CH_3 (di-methyl sulfide, DMS) and CH_3-S-S-CH_3 (di-methyl disulfide, DMDS). For reporting purpose, the sum of all organic sulfur gases is reported as organic sulfur. For quantifying the amount of gases, gas samples were collected from the headspace of the sample bottles and measurements were conducted with cyro-trapping and gas-chromatography.

3.3 Results and discussion

3.3.1 The relationship between biopolymer and dewatering:

Protein in anaerobic & aerobic sludges **-** The results in Table III-2 indicate that during anaerobic digestion, biopolymer is released from the sludge matrix and this is consistent with the investigations of Novak et al (2002) and Park et al (2004). During this study, it was observed that polysaccharide and protein concentrations approximately doubled following thermophilic anaerobic digestion. For mesophilic digestion, protein was found to increase about 25 % in Phase -I and 12 % in Phase-II, but polysaccharide declined comparatively.

Protein in sequentially anaerobic-aerobic digested sludge was found to decrease (Figure III-1), and this is consistent with results from Park et al (2004). It was observed that at three day aerobic digestion more than 50% of the protein was removed. Average protein removal after 6 day aerobic digestion of thermophilic digested sludge was measured to be 88%, while that for mesophilic digested sludge was observed to be 65%.

Table III-2 – Summary of biopolymer and solids in different digesters during two operation phases.

Sludge		**TS%**	**VS%**	**VSR%**	**Protein**	**Polysaccharide**
					(in mg/L)	
Phase -1	Feed	3.9	3.3		1,030	280
	Th-20	2.1	1.6	51.6	2,370	650
	ThAer6	1.6	1.2	64.4	200	280
	Me-10	1.7	1.7	48.6	1,160	250
	MeAer6	1.3	1.3	60.2	470	250
Phase -2	Feed	3.6	2.7		770	160
	Th-15	3.4	2.2	20.2	2,370	300
	ThAer3	2.6	1.6	41.1	1,240	360
	ThAer9	2.5	1.4	48.6	360	160
	Me-15	2.2	1.3	51.5	1,290	160
	MeAer3	1.8	1.1	61.4	250	280
	MeAer9	1.6	0.9	67.5	350	100

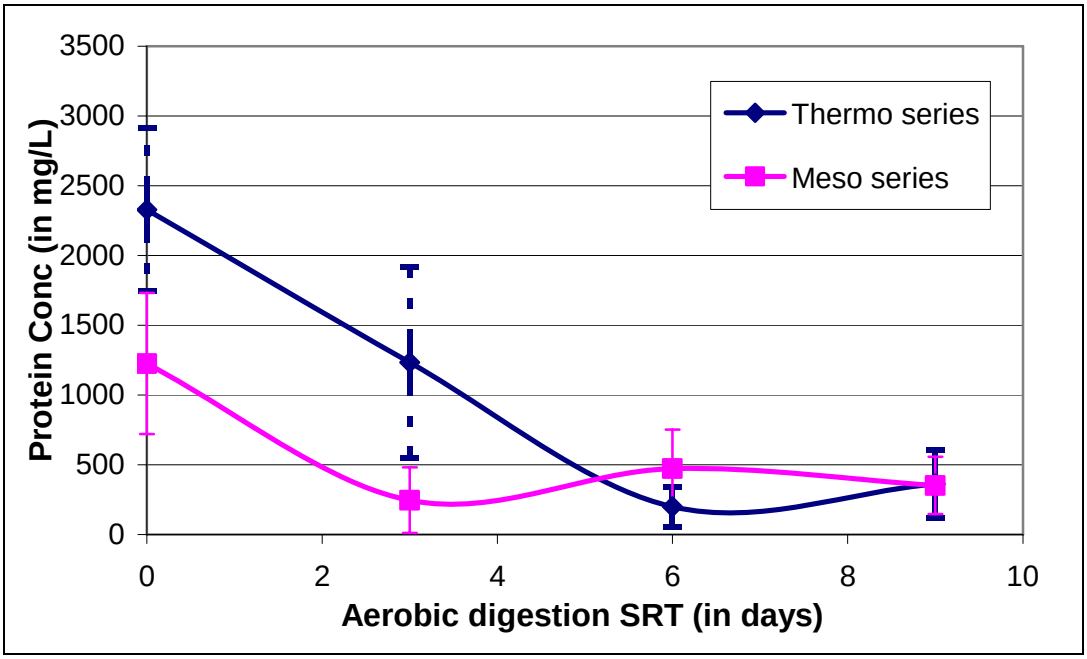

Figure III-1 – Protein concentration of influent and effluent of aerobic digesters. The influent from two different SRTs has been averaged to represent day 0 protein concentrations.

Polysaccharide accumulation and degradation **-** Figure III-2 shows the average polysaccharide concentration in the anaerobic digested sludge and in aerobic digesters for different digestion periods. The thermophilic digested sludges have higher polysaccharide concentration than the mesophilic sludges. In addition, the percentage removal of polysaccharides is higher for the thermophilic anaerobic–aerobic sequence (more than 60% after six days aerobic digestion). For the mesopilically digested sludge, the polysaccharide increase at both 3 and 6 days aerobic digestion and started declining afterwards. Novak et al (2003) showed that aerobic digestion releases polysaccharides into solution. It was thought that for the 3 and 6 days aerobic SRTs, release of polysaccharides exceeded polysaccharide degradation until day 9.

The polysaccharide accumulation in the thermophilic anaerobic digester may be due to several factors including the inability of the thermophilic micro-organism to degrade polysaccharide, or the high temperature environment, which results in a high release of polysaccharide from the sludge. An increase in the Calcium-ion and Magnesium-ion concentrations (Table III-3) during aerobic digestion suggests that Ca and Mg associated polysaccharide was released and this is consistent with the results of Novak et al (2003).

Thermophilic anaerobic-aerobic digestion shows better overall biopolymer removal than the mesophilic anaerobic-aerobic sequence (Figure III-3). Total biopolymer removal is more than 80% in the thermophilic sequence, while in the mesophilic anaerobic-aerobic sequence the maximum removal was 70%.

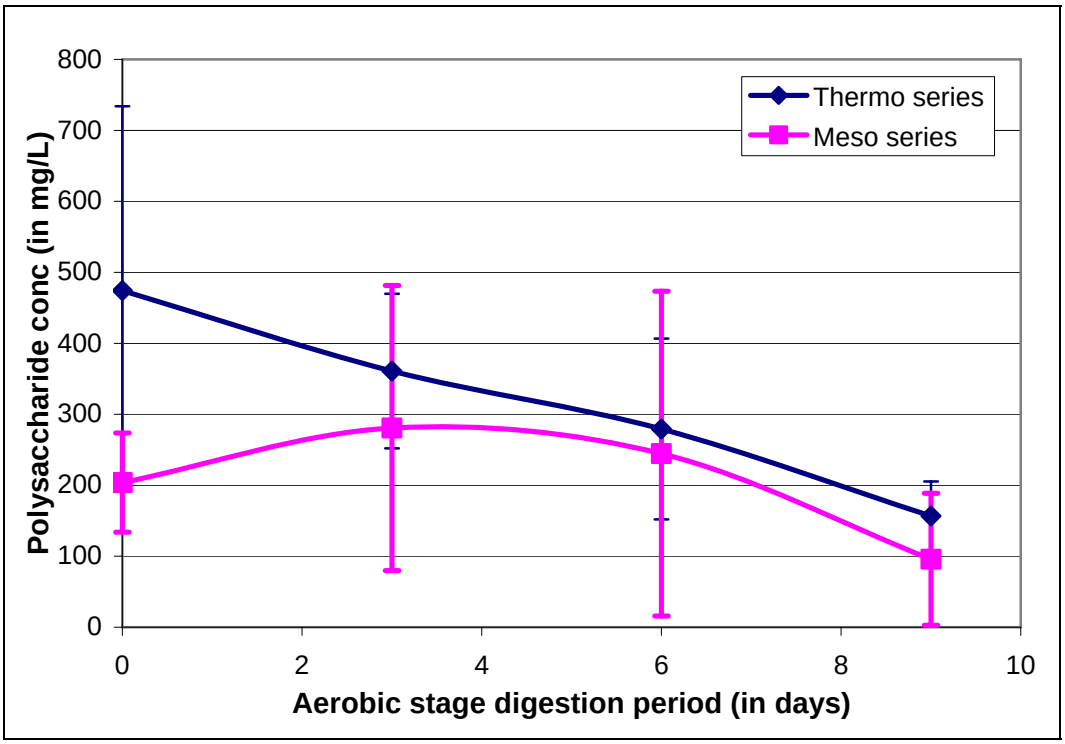

Figure III-2 – Polysaccharide conc. at different SRTs for mesophilic-anaerobic and thermophilic-anaerobic influent in the aerobic digesters.

CST and polymer dose requirement – The CST and optimum polymer dose measurements were conducted when the anaerobic digesters attained steady state. Figure III-4 and Figure III-5 shows the optimum polymer dose and corresponding minimum CST. Overall, the thermophilic anaerobic sludge had a lower CST and lower polymer dose requirement than mesophilic anaerobic digested sludge.

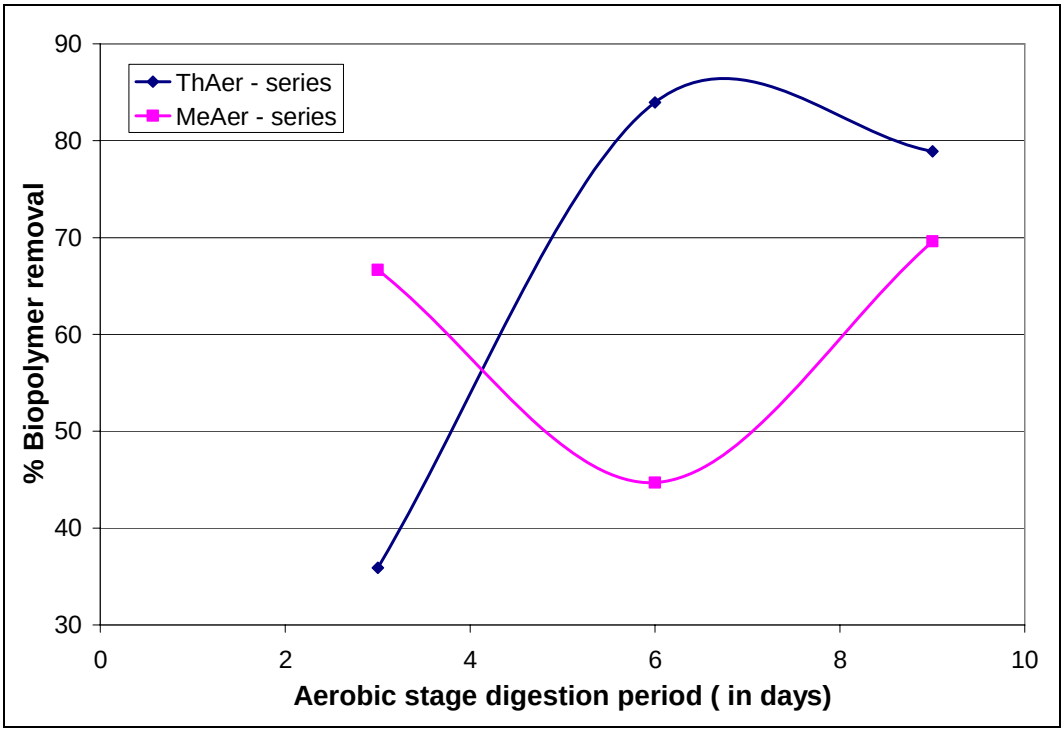

Figure III-3 – Comparison of Aerobic digestion SRTs and influent type on the total biopolymer conc. removal in the aerobic digesters.

A comparison of CSTs for anaerobic digested sludge and anaerobic-aerobic sequentially digested sludge (Figure III-6 and Figure III-7) suggests that a substantial reduction in the CST and optimum polymer dose took place due to sequential aerobic digestion at SRTs as low as three days. Figure III-8 suggests that low polymer dosage is required at optimum CST by thermophilic anaerobic-aerobic digested sludge (for aerobic digestion period of less than six days) than for mesophilic anaerobic-aerobic biosolids. From Figure III-7, it can also be interpreted that polymer requirement and CST decreases with increase in aerobic digestion SRT and dewatering quality of the effluent biosolids is comparatively better.

Higher CST and polymer dose are considered to be related with higher protein and polysaccharide. The results in this study show decrease in biopolymer during the aerobic stage of sequential digestion and support the decrease in the CST and polymer dose consumption.

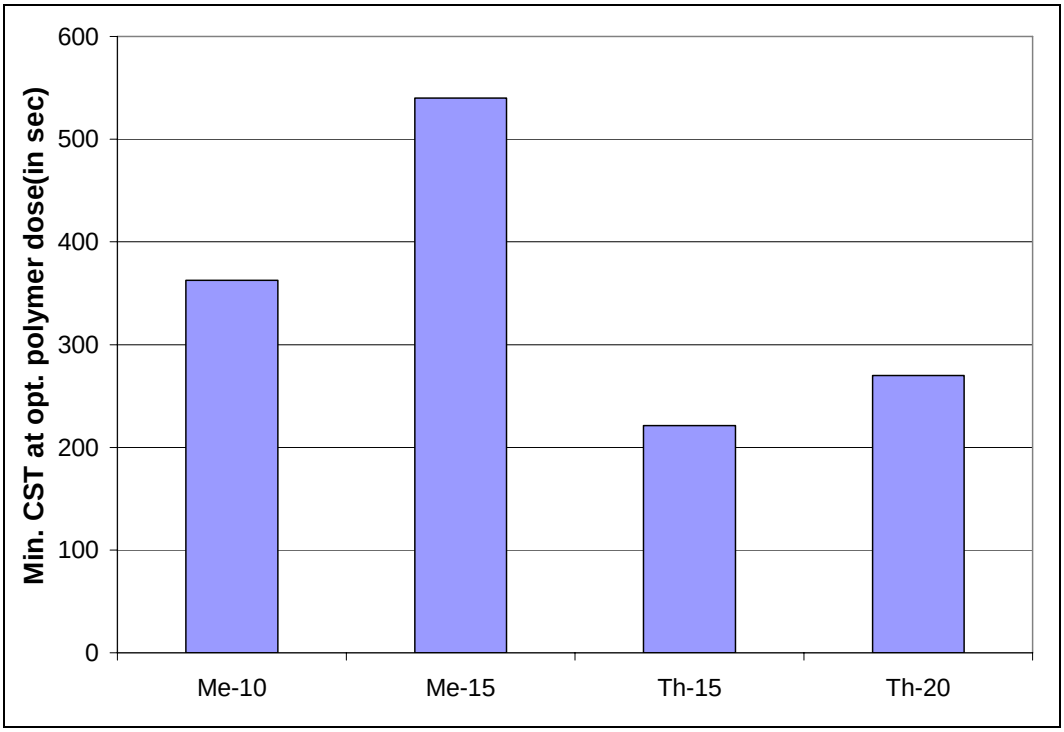

Figure III-4 – Comparison of Capillary suction time (CST) for the anaerobic digested sludges.

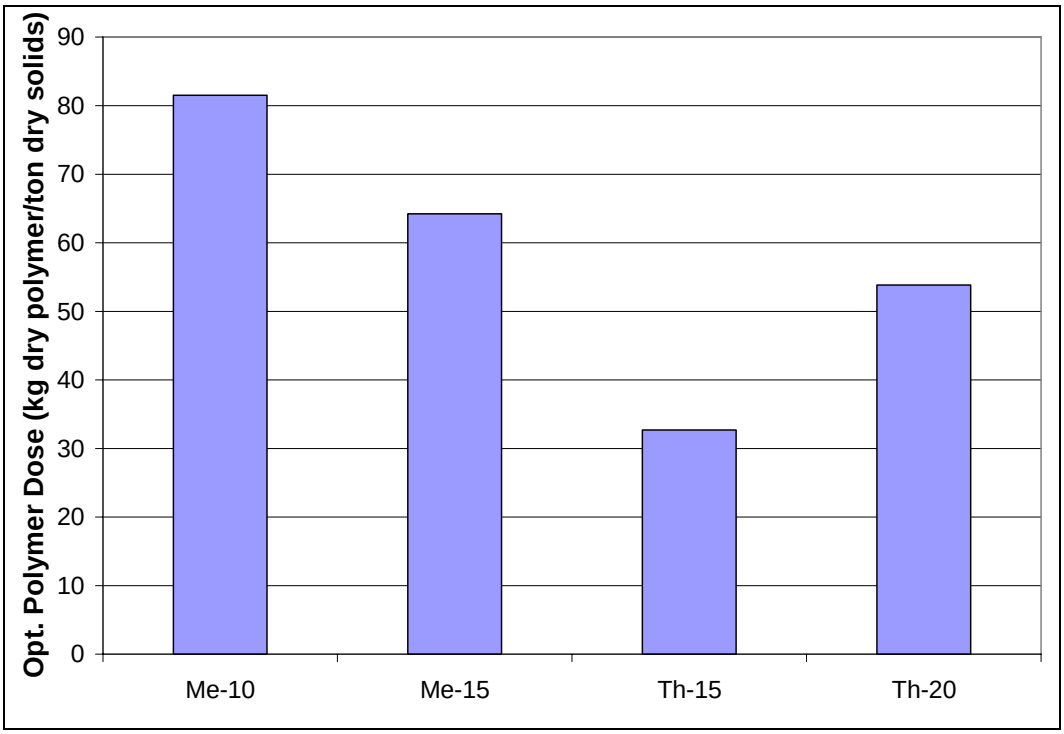

Figure III-5 – Comparison of polymer dose requirement for the anaerobic digested sludges. NOTE: Data for the Th-15 digester were collected during the poor performance period.

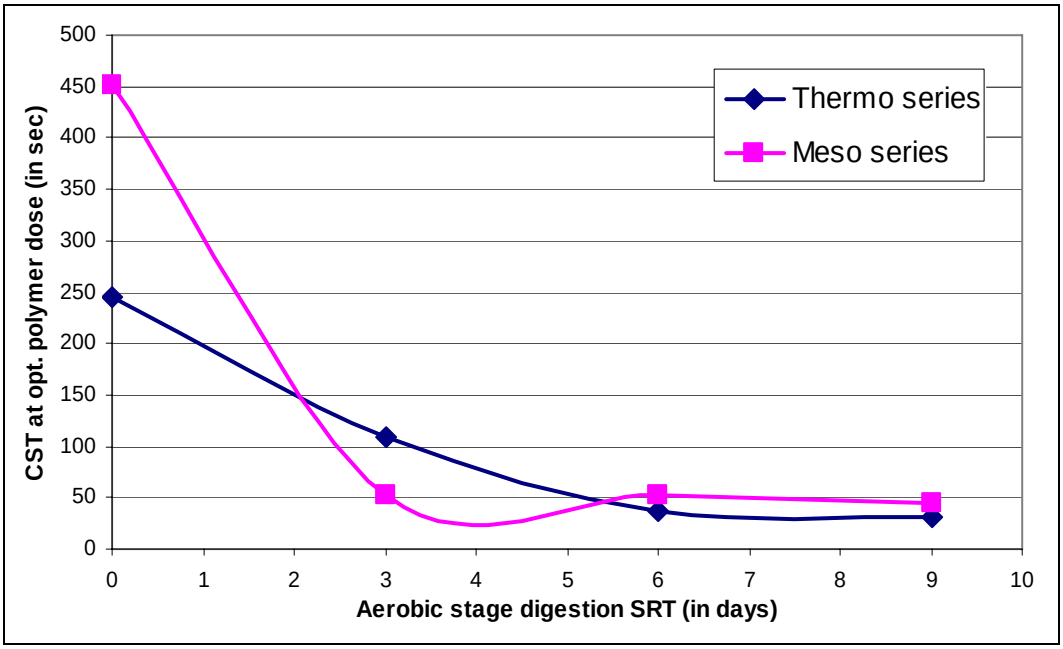

Figure III-6 – Effect of aerobic stage SRT and influent sludge in aerobic digesters on the CST. Day-0 data are the representative average value of CSTs measured for anaerobic digested sludges from different phases.

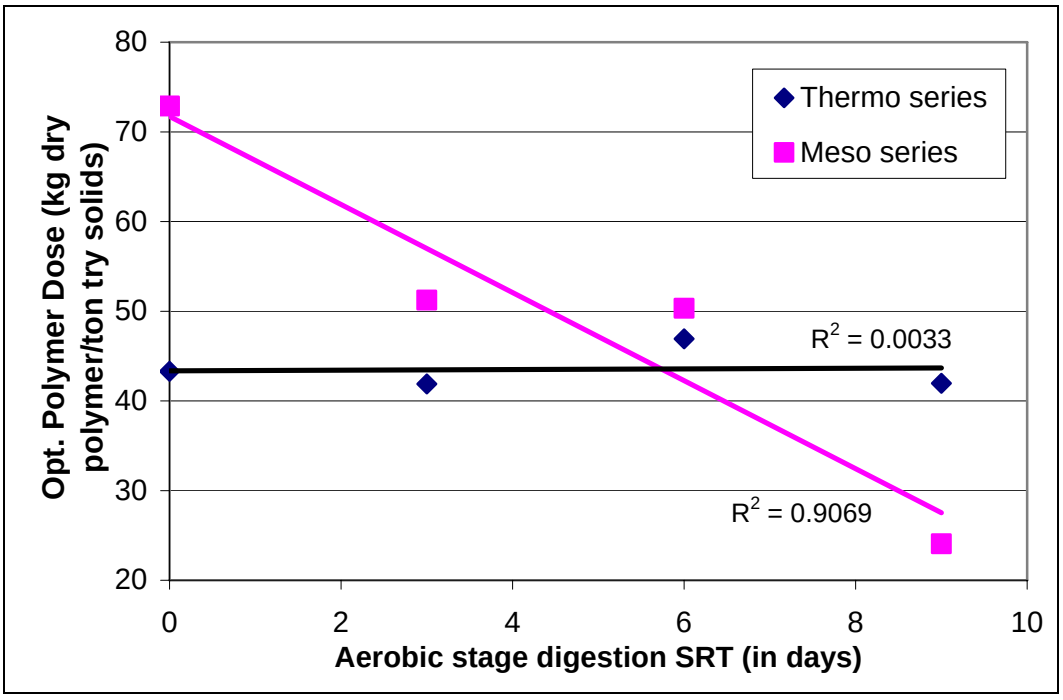

Figure III-7 – Optimum polymer dose requirement after the aerobic digestion and effect of influent sludge on the polymer requirements. Day-0 data are the representative average value of CSTs measured for anaerobic digested sludges from different phases.

Cation data (Table III-3) also support the inference about the improvement in dewatering following sequential anaerobic-aerobic digestion. Divalent cations are considered to be linked with polysaccharide and it was found that both divalent cations and polysaccharides are released in the system during the aerobic digestion. Comparison of change in divalent cation concentrations during aerobic digestion suggests that more cations are released for mesophilic influent which is consistent with a higher optimum polymer dose requirement. The increase in cations and simulations release & degradation of polysaccharides supports the hypothesis that two different fractions of solids are present in floc which is degraded during anaerobic and aerobic digestion.

Table III-3 – Cation concentration in different effluent sludges and comparison between ratio of sum of monovalent cations and divalent cations.

Sludge		Na^+	K^+	NH_4^+	Ca^{++}	Mg^{++}	M/D ratio	Solid cake	
		(in meq/ L)						TS%	VS%
Phase -1	Feed	2.2	2.4	12.9	9.9	3.5	1.3		
	Th-20	1.6	1.9	59.5	2.0	1.56	17.7	21.5	12.6
	ThAer6	2.1	2.4	7.9	7.8	2.5	1.2	18.8	11.8
	Me-10	1.7	2.1	52.7	3.7	2.6	9.0	24.4	13.8
	MeAer6	1.9	2.4	9.2	4.2	1.9	2.2	21.3	12.6
Phase -2	Feed	0.5	1.78	15.8	4.2	2.2	2.8		
	Th-15	0.5	1.7	52.8	1.4	1.8	17.5	32.5	23.2
	ThAer3	0.8	1.3	13.9	2.7	1.7	3.6	21.6	15.0
	ThAer9	1.6	1.4	4.2	4.9	1.8	1.1	23.0	16.4
	Me-15	0.5	1.9	48.7	3.3	2.1	9.6	17.8	11.7
	MeAer3	1.2	1.9	9.2	5.5	2.1	1.6	29.3	17.2
	MeAer9	2.6	1.8	2.2	9.1	2.6	0.6	27.0	15.7

3.3.2 Odor generation:

Effect of temperature and methanogenic activity on odor production – Adams et al (2004) in an odor generation study from anaerobically digested sludges from a variety of treatment plants found that odor generation from the dewatered biosolids depends upon the sludge characteristics and biosolid treatment train. One of the important conclusions from this study was that even for properly operating anaerobic digesters, odors were still present. It was concluded from this study

that anaerobic digestion was not guaranteed to produce low odor sludge. Therefore, since sequential anaerobic/aerobic digestion improves solids destruction, it was of interest to determine if sequential aerobic digestion could reduce odors.

Odors from the anaerobically digested sludges were measured using the headspace techniques of Novak et al (2003) and the peak odor concentration data from distinctly treated solids are presented in Table III-4. The data indicate that more odors are produced from the biosolids which were digested under anaerobic mesophilic conditions. In addition, the mesophilically digested sludge produced sulfur gases much more rapidly, peaking at day 7, compared to the thermophilic sludge which had a peak sulfur concentration at day 33. The thermophilic biosolids produce a low peak odor, but odors persist for about 40 days. The results are consistent with the WERF-II study (Adams et al, 2003) which also report higher odors for shorter duration from the mesophilic digested biosolids in comparison to the low odors for longer duration from the thermophilic digested biosolids. The main reason for difference in the odor generation profiles may be differences in the genre of sulfur reducing bacteria. It is thought that in thermophilic digested sludge, bacteria with the ability to convert the sulfur-containing amino acids, cysteine and methonine to mercaptans and dimethylsulfide are not as common as in the mesophilic digested solids, and due to this the organic sulfur peak usually appear later than that in the mesophilically digested sludges. In addition to this, thermophilic biosolids also lack bacteria with the capability which can fix organic-sulfur and that's why odor last for long period.

The data also support the hypothesis by Higgins et al (2003) that methanogens play an important role in odor removal by converting methane-thiol and other organic sulfur compounds to sulfide. High organic sulfur concentrations were measured in samples which were spiked with 5 mL BESA, the methanogen inhibitor (Table III-4, Figure III-10, Figure III-11 and Figure III-12), except for the Th-20 sample.

Role of Anaerobic and aerobic phase SRT – Investigation concerning the effect of SRT on odor generation suggest that an increase in the anaerobic phase digestion period reduces the odor

generation from the resulting biosolids. Figure III-8 and Figure III-11 present the effect of anaerobic SRT on organic sulfur with BESA addition. For the BESA amended samples, a higher SRT results in lower organic sulfur. The peak organic sulfur concentration in the BESA amended sludges is considered to be the odor potential of that sudge. In Figure III-9, the effect of the aerobic digester SRT is shown. It can be seen that for the thermophilic sludges, the aerobic SRT has little effect on organic sulfur gas potential while for the mesophilic anaerobic-aerobic sludges, the odor potential goes down as the aerobic SRT increases. This suggests that while the thermophilic anaerobic digester produces lower odor potential, the added aerobic treatment does little for additional odor reduction. In contrast, the aerobic treatment following mesophilic anaerobic digestion has a dramatic effect on odor potential. Figure III-9 and Figure III-12. shows that more than 20% odor can be removed from mesophilic digested biosolids just after 3 day of aerobic digestion and after 9 days of aerobic digestion 60% odor production potential can be reduced.

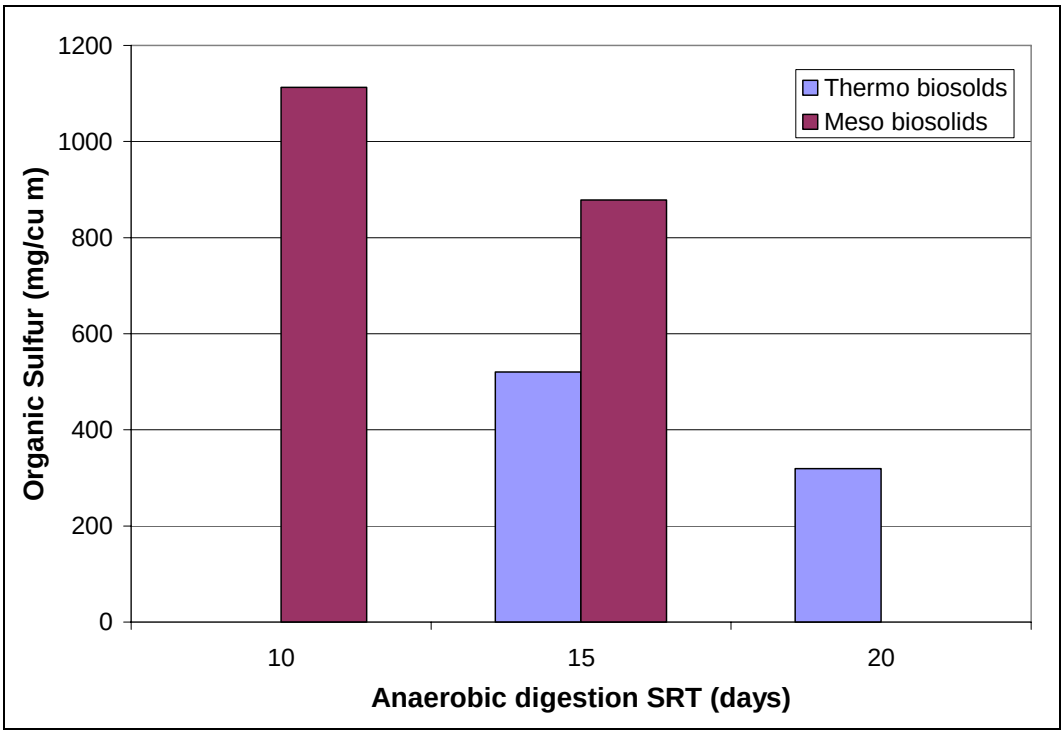

Figure III-8 - Odor potential (odors from BESA amended biosolids) changes as a function on anaerobic digestion SRT.

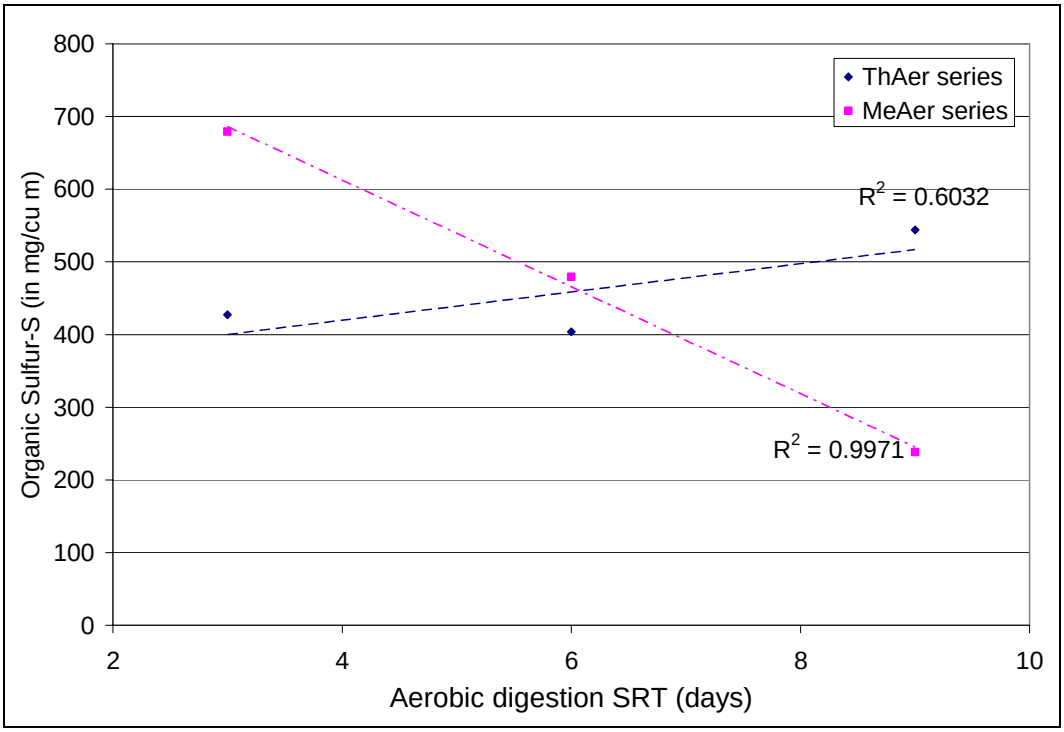

Figure III-9 - Odor potential changes in the sequentially anaerobic-aerobic digested biosolids as a function of aerobic digestion SRT. More dramatic change was observed for mesophilic sludge than thermophilic.

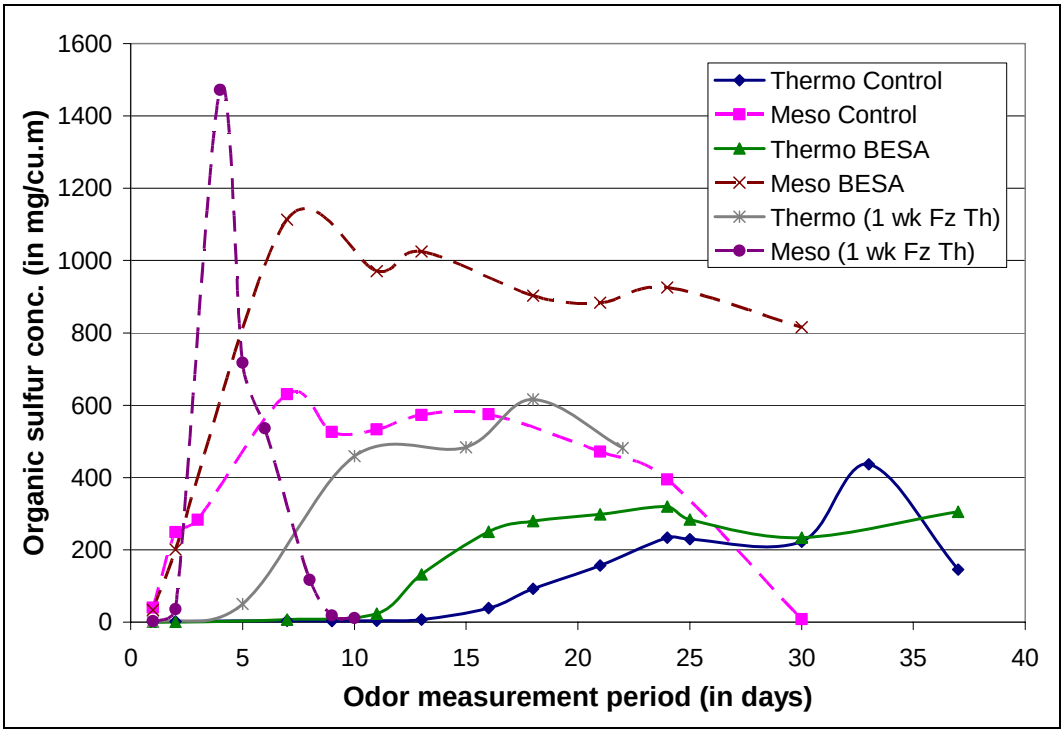

Figure III-10 – Comparison between the typical odor generation profiles of different anaerobic digested biosolids and effect of freeze-thaw on the odor generation from biosolids. (NOTE: FzTh – Freeze Thaw)

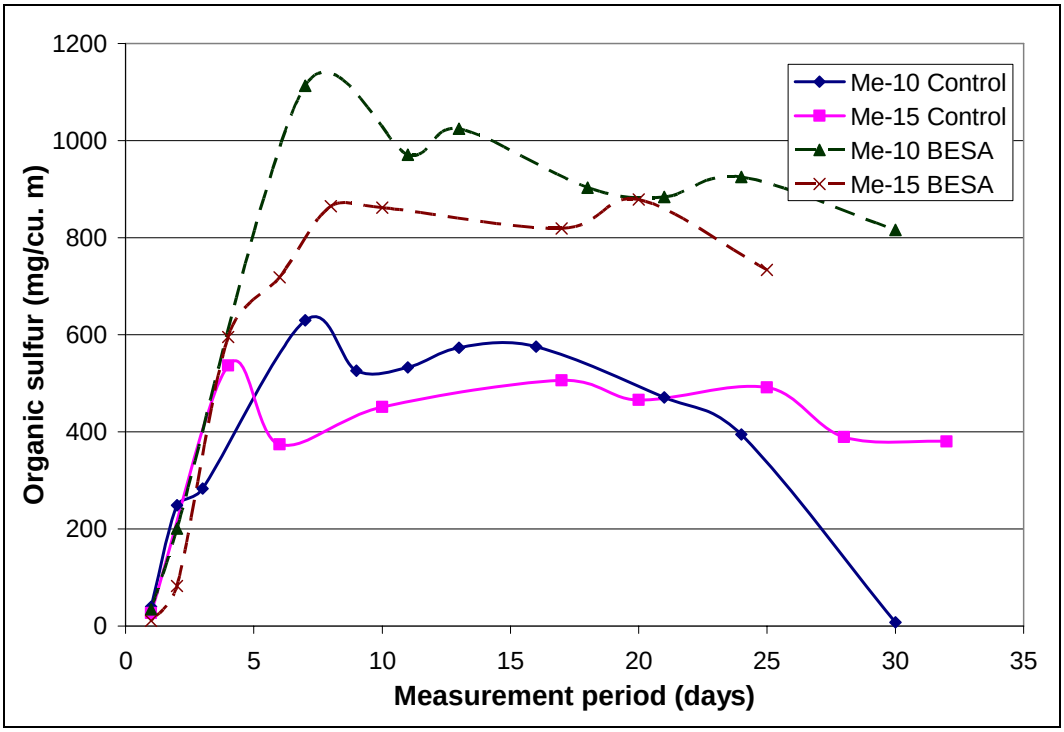

Figure III-11 – Comparison of organic sulfur concentration in Mesophilic digested biosolids and mesophilic biosolids spiked with BESA for inhibiting methanogenic activity in sample. High digestion period reduces the odors from the biosolids.

Effect of Freeze-thaw **–** Freeze thaw treatment of the biosolids samples was carried out to understand the effect of natural weather cycles on the odor production from the biosolids. The investigation suggests (Figure III-12, Figure III-13 and Figure III-14) that very high odors are produced upon thawing of biosolids which were frozen for a period of one week. Anaerobic thawed samples (frozen for one week) show an increase in organic sulfur of approximately 75% and the sulfur peaks appear in one to two days. In the sequential anaerobic-aerobic digested solids, (Figure III-12 and Table III-4) it can be seen that the additional aerobic digestion at low SRTs does little to reduce organic sulfur generation for the freeze thawed sludges. This is in contrast to the unfrozen sludges where aerobic digestion of mesophilically digested anaerobic sludge substantially reduces organic sulfur. It appears that during the freeze period, material is extracted from the sludge and is immediately biodegradable once the sludge is thawed, leading to a rapid production of sulfur gas. Odors from the solids digested anaerobically followed by three day aerobic digestion produced as high as 300% more odors. The longer aerobic digestion (SRT of 9 days) was found to produce lesser odors than the solids which were digested only for 3 days

(Figure III-14). This suggests that increase in SRT of second stage aerobic digester may help in will decrease the odor generation from the biosolids which may get exposed to freezing conditions.

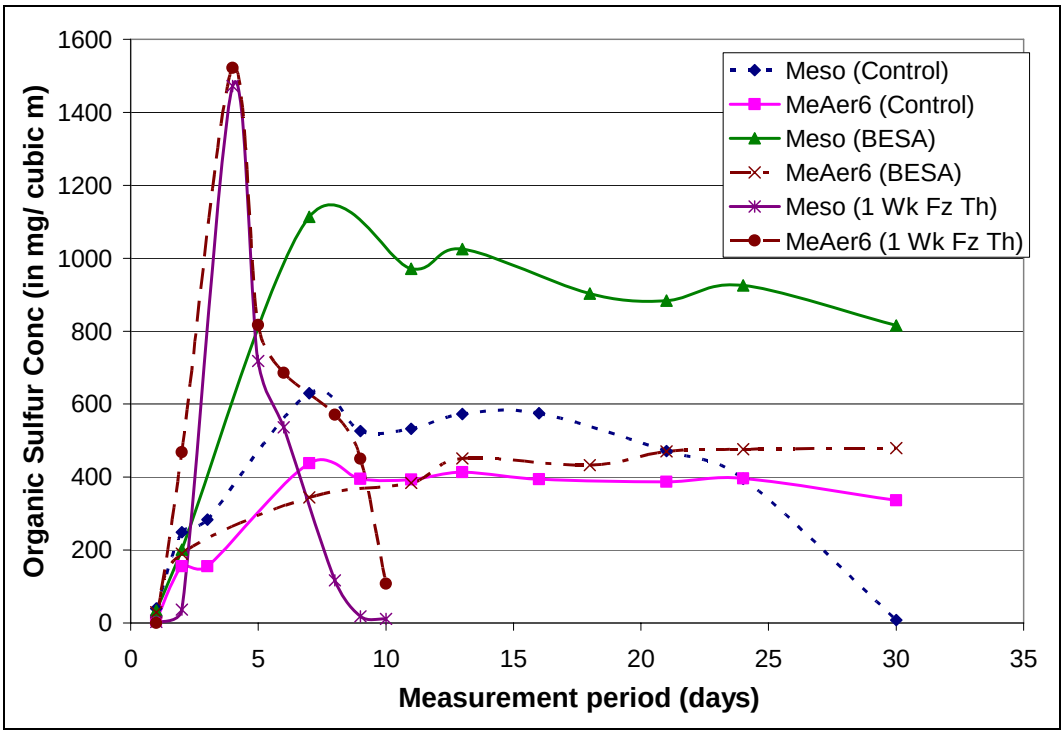

Figure III-12 – Comparison of typical odor production curve after only anaerobic digestion, sequential anaerobic-aerobic digestion and freeze thaw treatment of both anaerobic and anaerobic-aerobic digested samples.

Odor generation after one week freeze thaw treatment and one month treatment over thermophilic anaerobic-aerobic digested sludge differs from mesophilic anaerobic–aerobic sludge. Mesophilic anaerobic-aerobic digested sludge produced odor peak very fast, within 5 days after thawing for both one week and one month freeze thaw treatment, while thermophilic anaerobic-aerobic sludge peaks out after 5 days for 1-week freeze thaw and odor generation persists for more than 15 days after one month freeze.

Table III-4 - Peak organic sulfur concentration in biosolids samples prepared from different sludges and treatments.

Sludge	Un-amended	BESA	One week Freeze Thaw	One month Freeze Thaw	Digester Headspace odor
	(in mg/ cubic meter)				
Th-15	352	521	616	406	NA
Th-20	437	320	203	NA	15
Me-10	630	1,113	1,472	NA	2
Me-15	537	879	1,105	993	14
ThAer3	261	428	1,083	1,190	NA
ThAer6	244	404	395	NA	NA
ThAer9	295	544	515	1010	NA
MeAer3	205	679	743	419	NA
MeAer6	438	479	1,522	NA	NA
MeAer9	153	238	71	53	NA

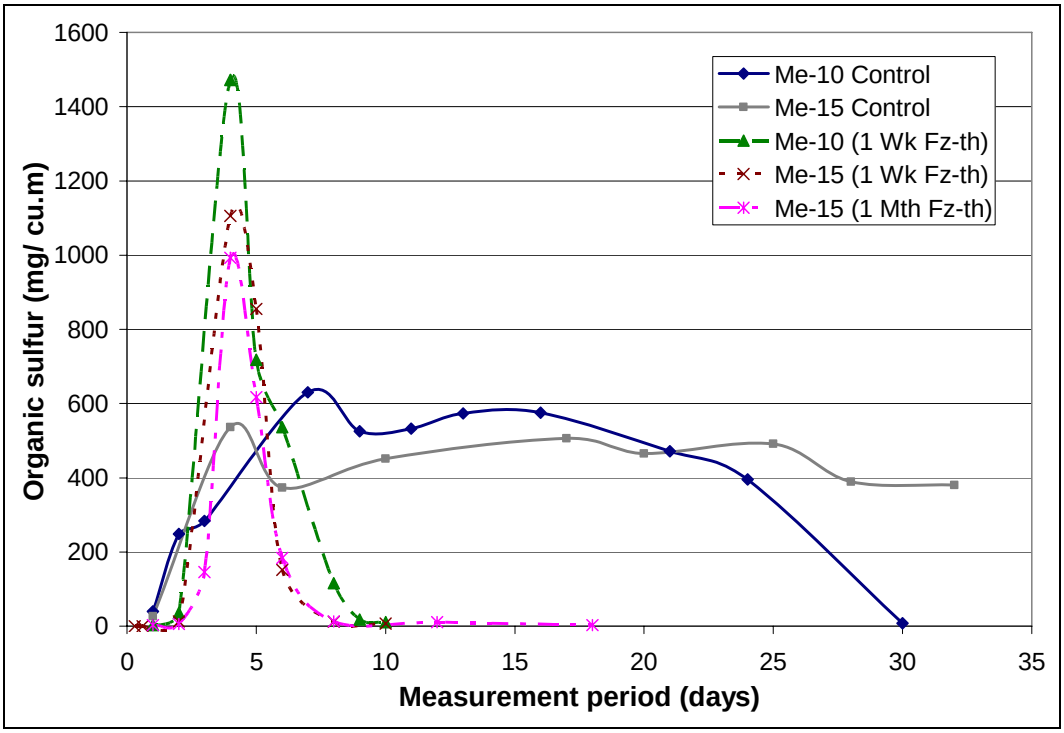

Figure III-13 – Effect of freeze-thaw period and digestion time on the odor production from biosolids samples.

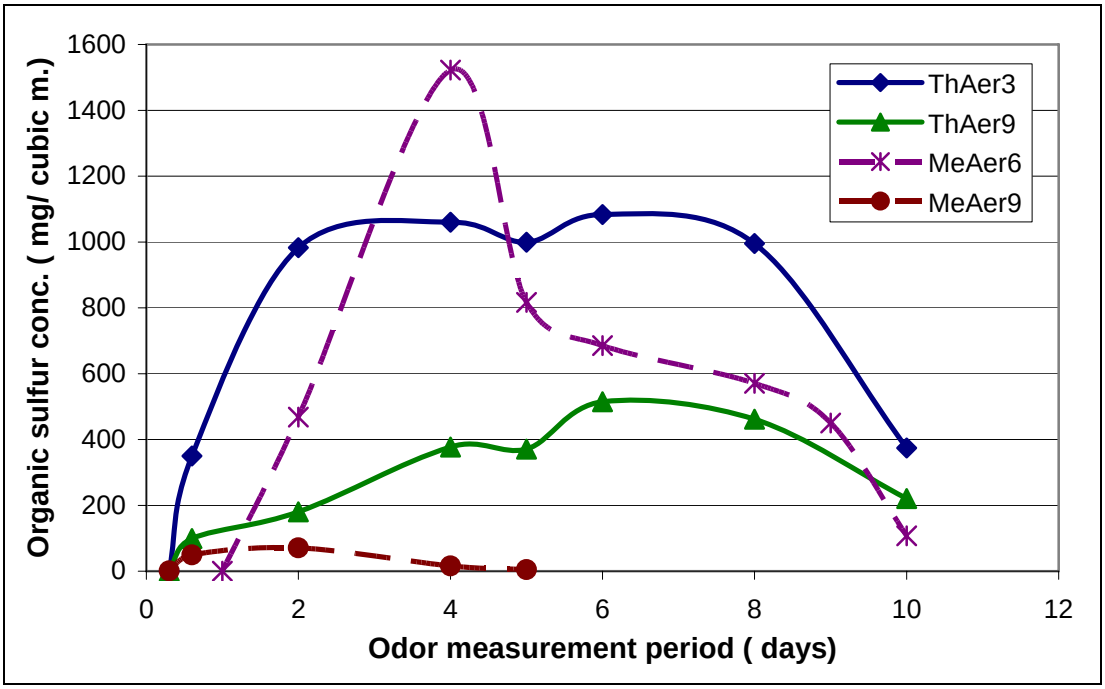

Figure III-14 – Effect on odor generation tendency of biosolids due to aerobic stage digestion period and influent sludge. The biosolids were treated under freeze-thaw cycle of 1 week.

3.4 Conclusions

The anaerobic-aerobic digestion of the sludge can improve the biosolids quality by improving the dewatering and odor generation from the biosolids. This study conclude that –

1. More than 50% biopolymer removal can be achieved after sequential anaerobic-aerobic digestion.
2. Improvement in the dewatering is supported by the reduction in the CST of the sequentially digested effluent and reduced polymer dose requirement. Decrease in the polymer dose requirement for the mesophilic digested effluent was 50% after the aerobic digestion, more than thermophilic digested effluent.
3. It was found that odor generation decreases with increase in the anaerobic digestion period as well as aerobic digestion SRT. 5 day increase in anaerobic digestion SRT was found to reduce approximately 20% odor potential of anaerobic biosolids. Addition 25% decrease was observed in odor potential of mesophilic digestion solids after 3 day of aerobic digestion and this increase up to 75% after 9 days of aerobic digestion of mesophilic biosolids.

4. Thermophilic biosolids generate 50% lesser odor in comparison to mesophilic biosolids, but the odor production period last longer than that for mesophilic biosolids.
5. Freeze-thaw cycle make more biopolymer available for the microbial activity, which is followed by increased odor generation after the thawing of biosolids. The odor generation period for freeze-thawed biosolids was found to be 4-5 days.
6. Prolonged aerobic digestion seems to reducing the odors from the biosolids, which undergo freeze-thaw cycle. Solids digested for 9 day were found to produce 50% lesser odors after freeze thaw than those were digested only up to 3 days.

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Appendix A

Research Note: Role of nitrate and nitrite in Volatile solids and nitrogen removal via denitrification in sequential anaerobic-aerobic digestion of solids

Kumar, N and Novak, J.T

Abstract

During an investigation of anaerobic-aerobic sequential digestion of solids, it was observed that more than 50% ammonia was lost from the system and no appreciable nitrite and nitrate concentration was measured. This batch study was designed to investigate the role of denitrification during the aerobic digestion of anaerobic digested sludge. Anaerobic digested sludge was spiked independently with different nitrate and nitrite concentrations in separate batches. During the study, no nitrite and nitrate was observed during the first three days of the digestion and more than 60% ammonium was found to be removed along with 80 % VFA from the systems. The role of nitrite and nitrate in VS & TKN removal was also investigated. Nitrite was found to assist in VS removal and TKN removal more than the nitrates.

Key words: Nitrification, denitrification, anaerobic-aerobic treatment, nitrite and nitrates.

A.1 Introduction

Nitrogen recycle from dewatered sludges following anaerobic digestion is one of the major nutrient loads for wastewater utilities that practice anaerobic digestion. During anaerobic digestion proteins are released from the sludge mass and ammonia is generated upon the degradation of protein. The biosolids after anaerobic digestion are usually dewatered and the water extracted during the process is re-introduced back at the head of the wastewater utility. The recycled water usually has very high nitrogen content and exert extra load on the upstream wastewater treatment processes.

Advance methods to remove the nitrogen from the wastewater have been engineered including the SHARON^{TM} process and anaerobic-aerobic sequential treatment for nitrogen removal. These processes have disadvantage of loss in alkalinity and an additional carbon source is required during the denitrification process. Bernet et al (2000) and Wang et al (2004) studied the nitrification process and suggested that nitrification can be optimized by controlling the DO, temperature (Hellinga et al, 1997) and SRT (Pollice et al, 2002). Chung et al (2002) suggested that partial nitrification (stopping at nitrite) can provide the shortcut for the biological nitrogen removal process and help in saving 25% energy required for aeration during nitrification.

Akunna et al (1993) suggested that the carbon source has also important role in the reduction of nitrite and nitrate with anaerobic sludge. The authors proposed that in the presence of lactic and acetic acid, reduction of nitrite and nitrate was 100% due to denitrification, but in the presence of glucose and glycerol dissimilatory nitrate reduction to ammonia (ammonification) was major nitrate/nitrite reduction pathway. In the same study, it was also suggested that the COD requirement for nitrate and nitrite reduction in the presence of acetic acid was higher than that in presence of glycerol and glucose. In another study (Murray et al, 1975) it was observed that nitrification occurred at higher rates when nitrite was the electron acceptor rather than nitrate. Bernet et al 2000 found that denitrification can take place during the filling period of aerobic SBR reactor, when mixed liquor had low dissolved oxygen levels.

Prior to this study, an investigation was conducted of anaerobic-aerobic sequential treatment to attain higher volatile solids (VS) removal and nitrogen removal. During the investigation, it was found that more than 50% nitrogen loss occurred and could not be accounted by considering nitrogen assimilation into the cells, nitrification and ammonia stripping. Denitrification was believed to be a major nitrogen removal process in the system, but no additional carbon source was required and no extra alkalinity addition was required. The aims of this study were to further investigate the nitrogen removal mechanism and the role of nitrite and nitrate during the aerobic digestion of anaerobic digested sludge. This was done by batch addition of nitrite or nitrate to

sludge from the aerobic reactor and following the investigation of VS, fatty acids, nitrate and nitrite fate during the process.

A.2 Methods and Materials

A.2.1 Batch bioreactor for nitrogen removal studies:

To understand nitrogen removal in the aerobic phase, a batch aerobic digestion process was carried out by spiking the batch digesters with different concentrations of nitrite and nitrate. The batch aerobic digestion study was conducted using mesophilic digested biosolids as feed. The mesophilic sludge was collected over a period of a few days from a digester maintained for another study and the sludge was stored at 4 ^{o}C. For investigation purposes, the stored sludge was spiked independently with three different concentrations of either nitrite or nitrate. Concentrations used for spiking the sludge were 10 mg/L, 30 mg/L and 50 mg/L (all as NH3) and a control was also maintained for comparison. Samples were collected from the digesters at the 3rd, 6th, 9th and 15th days of digestion. Volatile solid reduction, pH, VFA, TKN and total ammonia and soluble ammonium ion concentrations were measured. The dissolved oxygen (DO) concentration was maintained at 2 ppm during the operation period of the digesters.

A.2.2 Analytical methods:

For VFA and selected ion measurements (NH_4^+, NO_2^-, and NO_3^-), samples were centrifuged at 10,000 g for 20 min at 25 ^{o}C followed by filtration through a 1.5 µm glass fiber filter. The filtered samples were frozen and then thawed at room temperature prior to the analytical measurement. Thawed samples were centrifuged at 5,000 g for 10 min and filtered using a 0.45 um filter.

For VFA samples analysis, 900 µL samples were acidified by adding 100 µL phosphoric acid. Samples were analyzed using a Shimadzu GC-14-A gas chromatograph with a flame ionization detector. Helium, nitrogen, and hydrogen were the main gases used for analysis purpose. Air was used for makeup purposes. Flow rates of the different gases were as follows:

5. Helium – 17 mL/min

6. Nitrogen – 13 mL/min,
7. Hydrogen – 45 mL/min, and
8. Air – 450 mL.

Cation and anion concentrations in the samples were measured using a Dionex D-120 ion chromatograph (Dionex Corp., Sunnyvale – CA). For cation measurements, a CS-12 column equipped with conductivity detection and a self generating suppression of eluent was used. 20mM methanesulfonic acid was used for eluent at a 1mL/min flow rate, while for anion measurement AS9-HC column was used with an AG9-HC guard column.

Total solids, volatile solids, pH, DO, TKN, and total dissolved ammonia were measured according to Standard Methods (APHA 1999).

A.3 Results and Discussion

For measuring the denitrification activity and effect of the nitrate/nitrite concentrations, correlations between the different parameters were investigated. It was observed that nitrite and nitrate effect the TKN removal, volatile solid removal and ammonium removal during the aerobic digesters.

A.3.1 Effect of nitrate and nitrite on nitrogen removal

Figure A-1 and Figure A-2 present the TKN concentrations during aerobic digestion. The data suggest that addition of nitrite and nitrate have little impact on TKN removal.

The spike studies did, however, suggest that addition of nitrite and nitrate positively influence ammonium ion removal. Non-spiked control aerobic digesters showed less ammonium-ion removal from the system (Figure A-3 and Figure A-4). It can also be interpreted by comparing Figure A-3 and Figure A-4 that during the initial period of the aerobic digestion that ammonium-ion removal took place at an approximately equal rate, independent of nitrate or nitrite spikes.

The lack of impact on the rate of TKN removal can be explained by the change in the protein concentration during the aerobic digestion. The protein concentration was found to decrease over the digestion period. Protein degradation is associated with organic nitrogen release and an increase in the ammonia in the system. It was found that rate of protein degradation was comparatively high between the 3rd and 9th day of aerobic digestion. Hence, it can be assumed that simultaneous TKN removal and addition was taking place during aerobic digestion.

The VFA concentration (Figure A-5) in the nitrite-spiked systems was measured and it was found that during the first three days of digestion, 80% of the VFA was removed from the aerobic digesters. Akunna et al (1993) investigated the role of the carbon source in the nitrite and nitrate reduction and found that non-fermentative carbon sources favors denitrification, while fermentable carbon sources favors the ammonification of the nitrite and nitrates. During the current studies, measurement of the nitrite and nitrates was also done, but until the 9th day of the operation no nitrite and nitrates were present. Correlation between the VFA and ammonium-ion suggests that that VFA was utilized as a carbon source during the simultaneous nitrification and denitrification in the aerobic digester, as shown in Figure A-6.

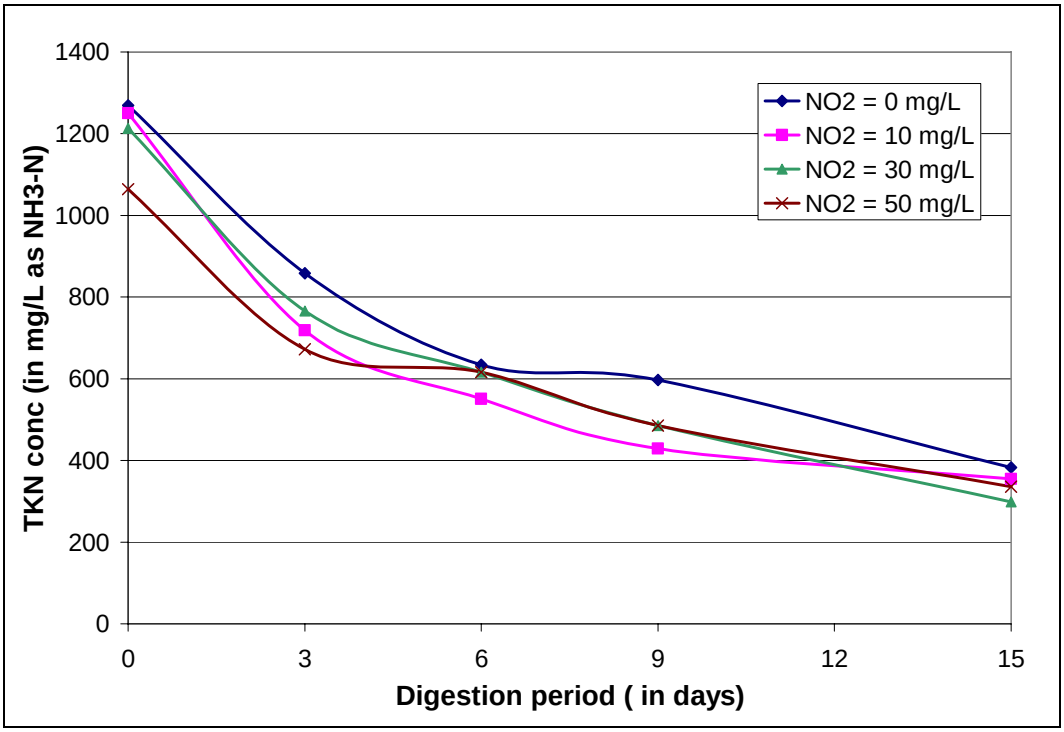

Figure A-1 – Effect of nitrite spike on TKN removal with digestion period.

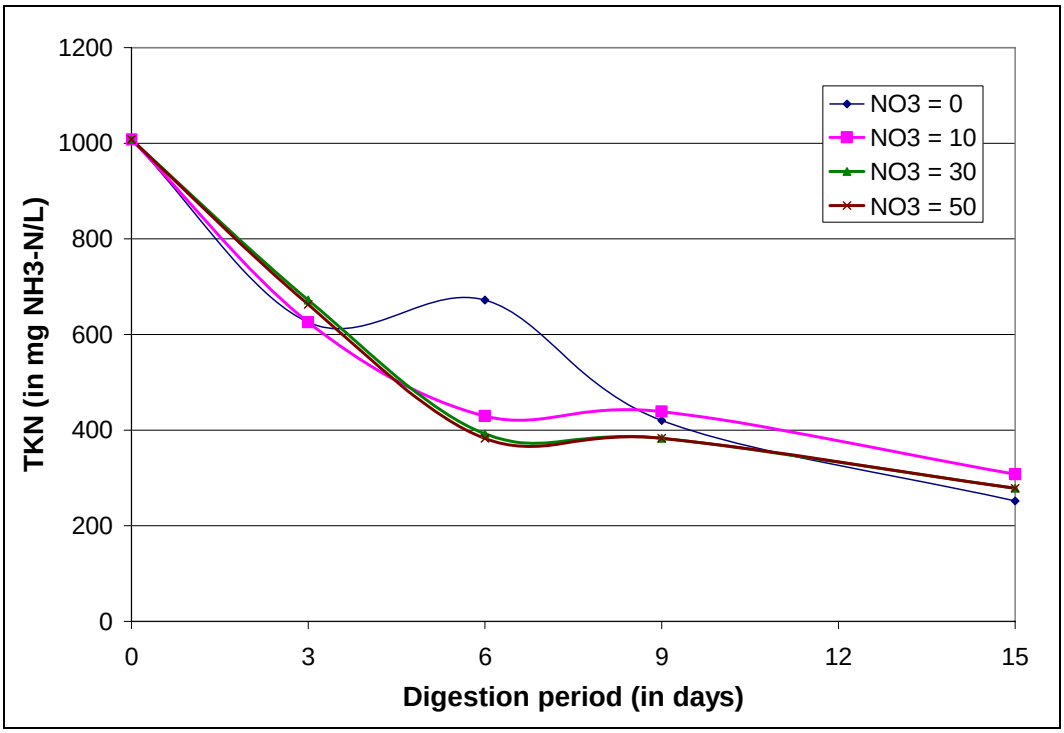

Figure A-2 – Effect of nitrate spike on the TKN removal during the aerobic digestion.

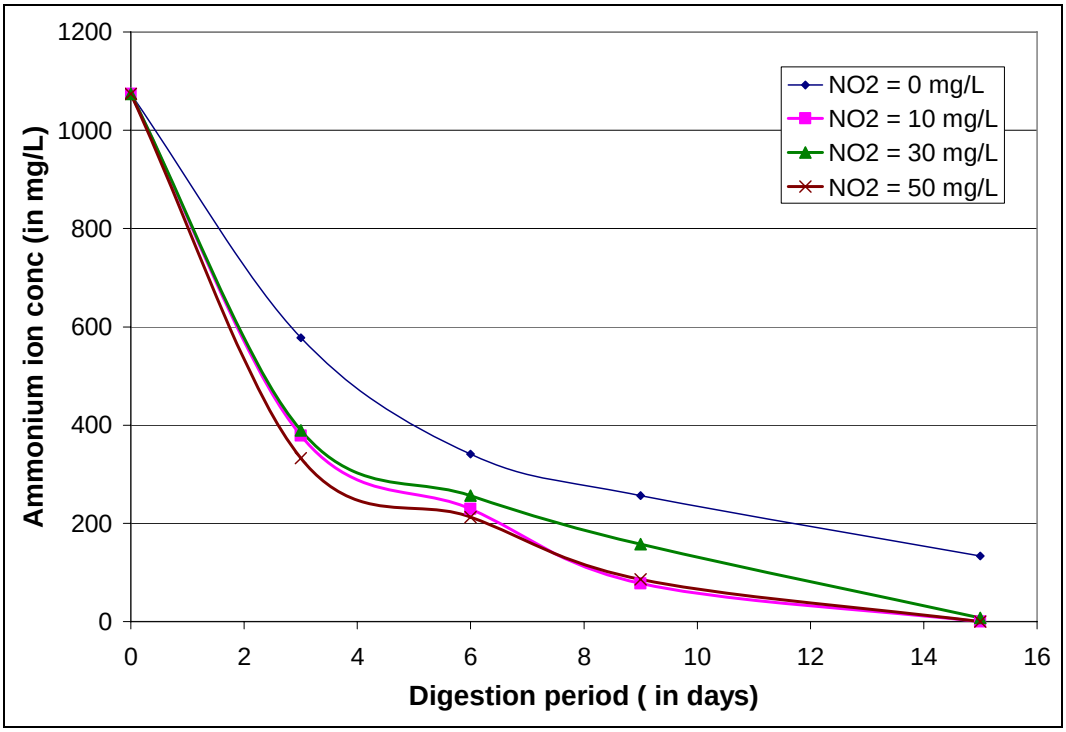

Figure A-3 – Change in ammonium conc. during aerobic digestion and effect of nitrite spike on removal

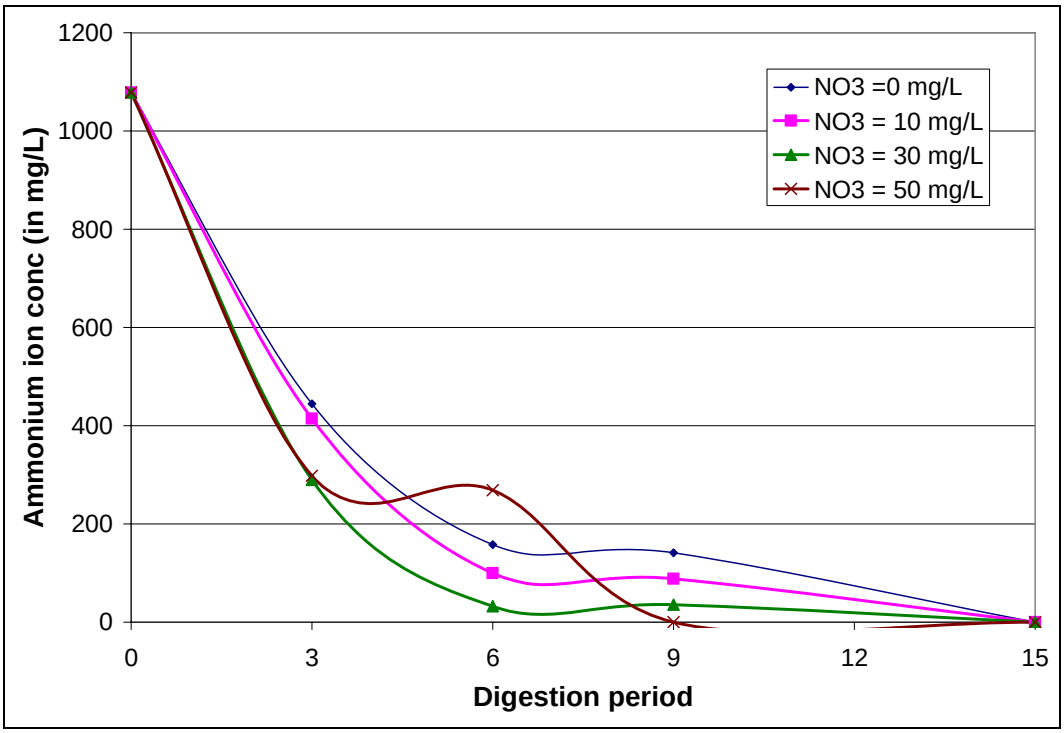

Figure A-4 – Effect of nitrate conc. on the ammonium removal from the aerobic digester at different SRTs.

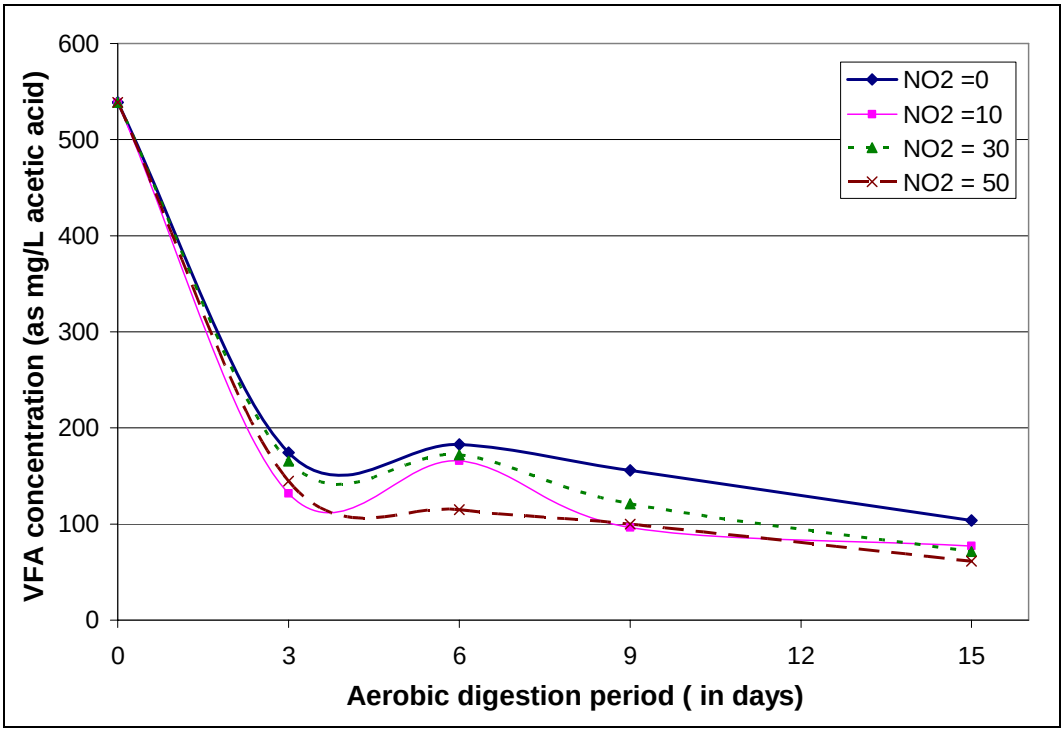

Figure A-5 – Volatile fatty acid removal during the aerobic digestion. Approximately 80% removal was measured at 3rd day of the operation.

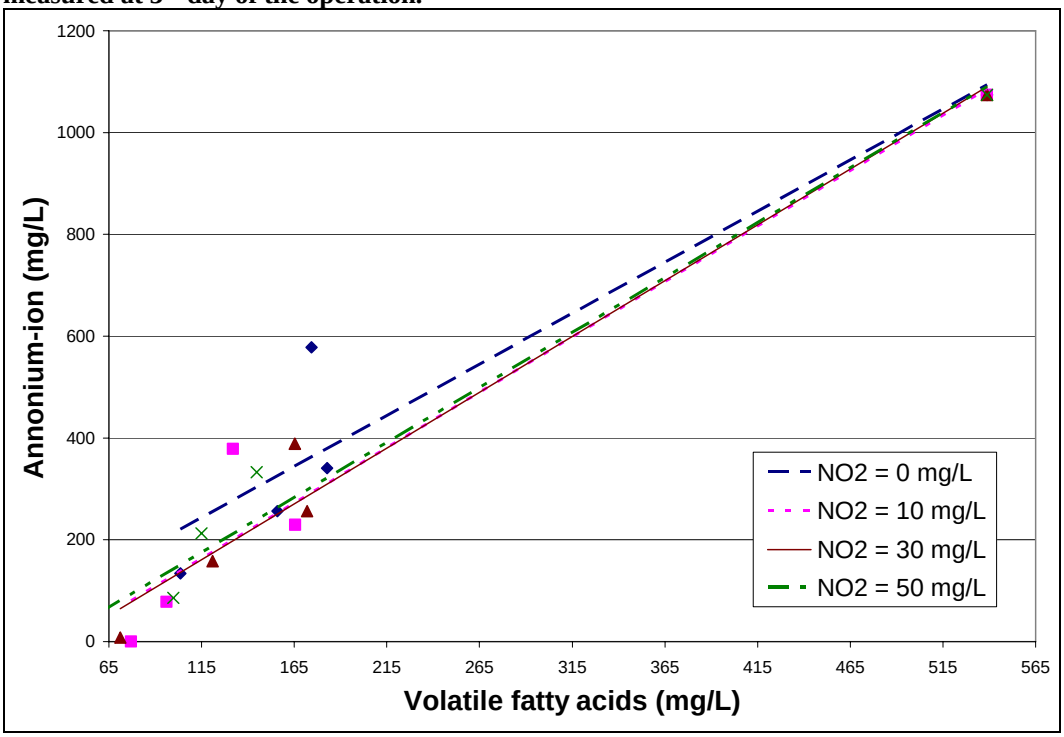

Figure A-6 – Correlation between the ammonium–ion during aerobic digestion and corresponding volatile fatty acids concentrations. All linear correlation had R^2 greater than 0.9.

A.3.2 Effect of Nitrate and Nitrite on pH

During the study it was found that during the initial digestion period the pH increase and than continuously decrease. It was observed that the pH was greater in the spiked digesters than the non-spiked digesters. The maximum and minimum pH values were higher in the digesters spiked by nitrite (Figure A-7) than the corresponding maximum and minimum pH values measured in nitrate spiked digesters (Figure A-8).

The increase in pH during the first three days can be explained by the loss of volatile fatty acids and denitrification which were taking place in the digester simultaneously. Alkalinity produced by the de-nitrification process along with simultaneous loss of volatile fatty acids caused a decrease in acidity. In both nitrate and nitrite spiked batch aerobic digesters, the pH was observed to decrease after 3 days of aerobic digestion. The reasons for pH decrease are not explicitly clear from the data.

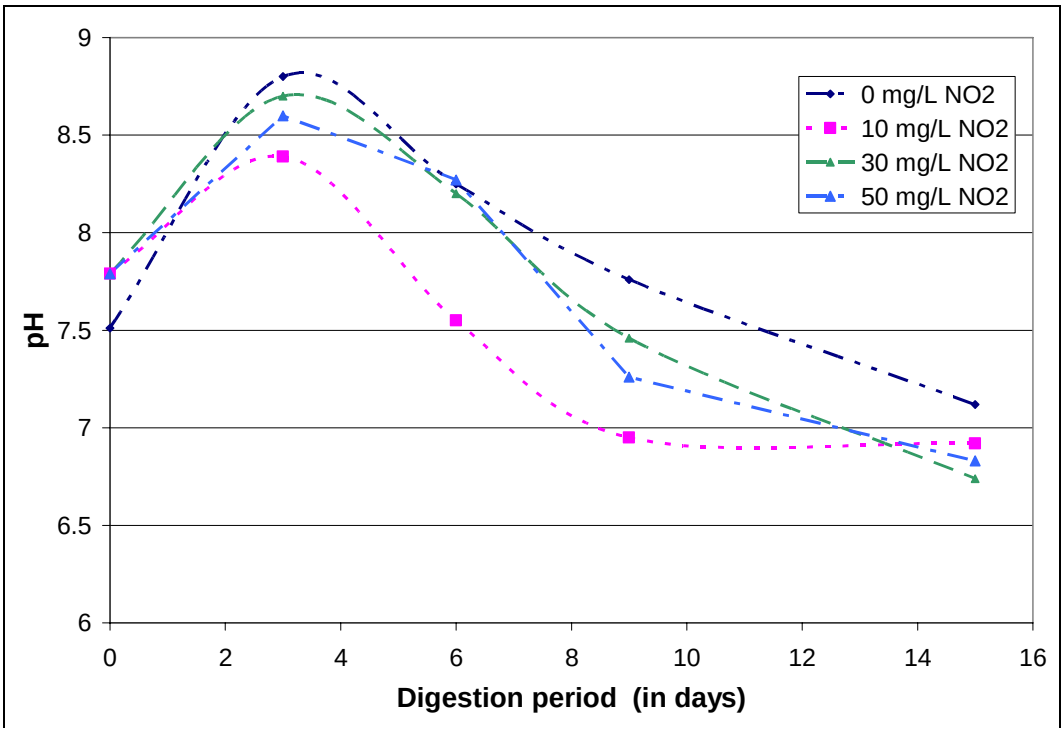

Figure A-7 – pH profile during the aerobic digestion of the anaerobic sludge spiked with nitrite.

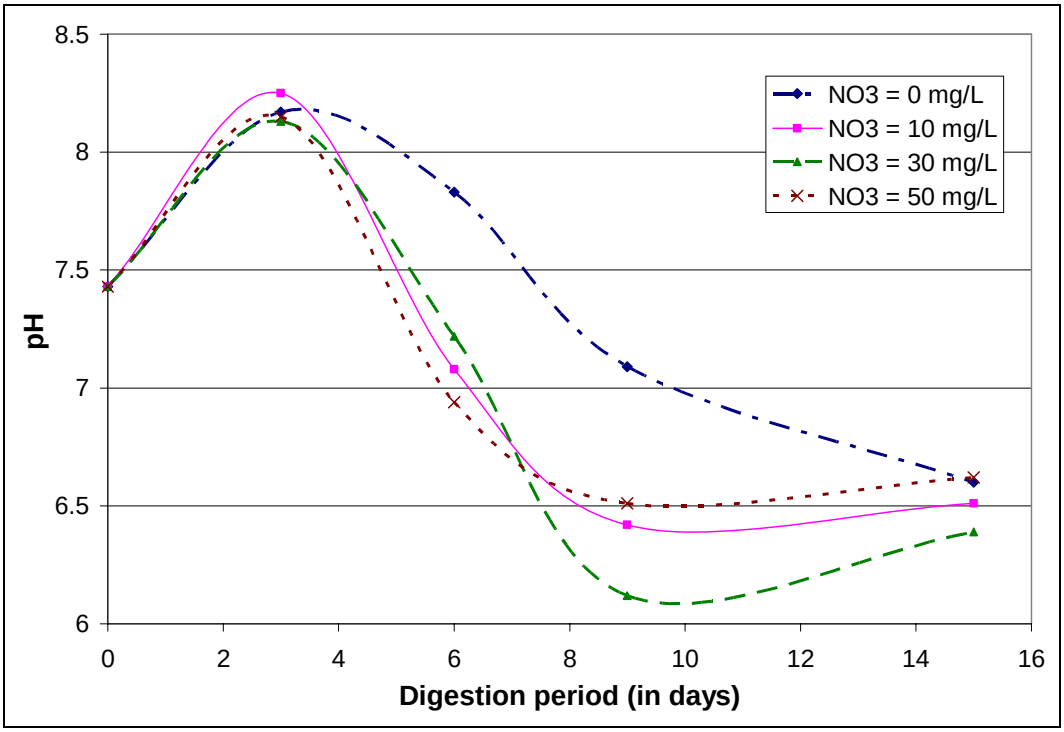

Figure A-8 – pH profile of the different digesters spiked by nitrate during aerobic digestion.

A.3.3 Effect of nitrate and nitrite on volatile solids reduction

Volatile solids removal (VSR) at different SRTs was also monitored in the nitrate and nitrite spiked digesters. It was found that nitrate spiked sludge showed more volatile solid removal during aerobic phase digestion. More volatile solid reduction was measured in the digesters spiked with higher nitrite concentration (30 mg/L and 50 mg/L). Figure IV-9 shows that a strong correlation exits between VSR and digestion period.

Data collected from the nitrate spiked digester suggest that presence of nitrate slowed down volatile solids reduction and even after 15s day of aerobic digestion, the volatile reduction in nitrite/nitrate spiked the digesters remain lower than volatile reduction in non-spiked digester (Figure A-10), although the difference in the VSR between spiked and non-spiked samples was not appreciable.

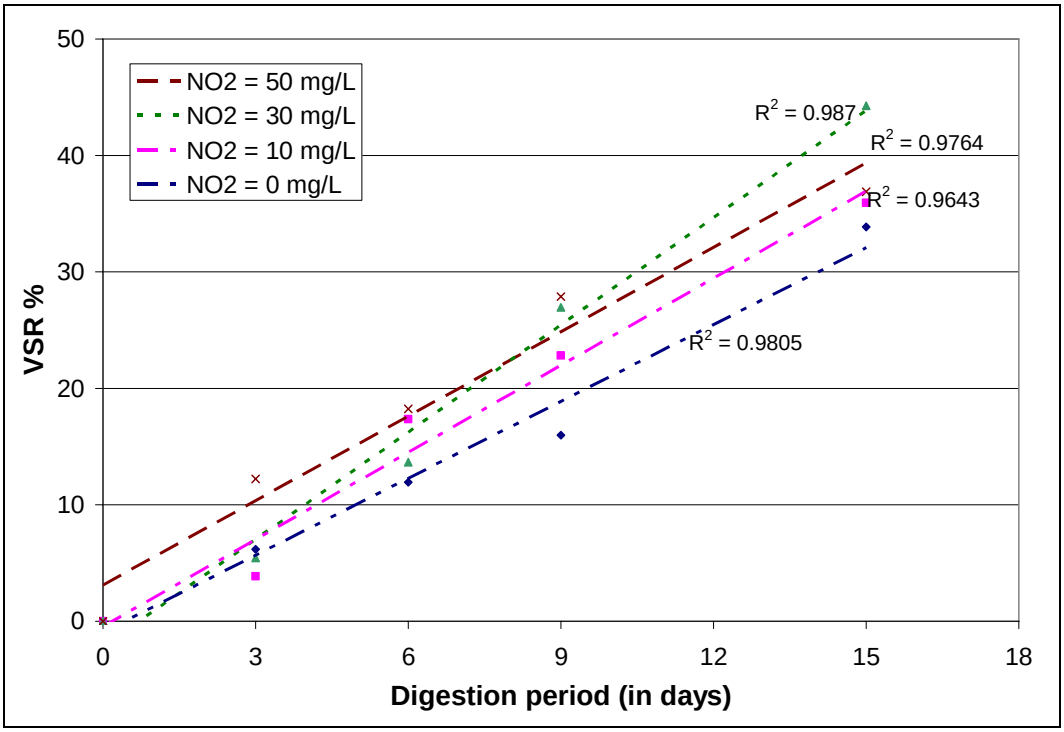

Figure A-9 – Effect of nitrite spike on volatile solid removal during aerobic digestion. Linear correlation curve shows strong relationship between VSR and SRT.

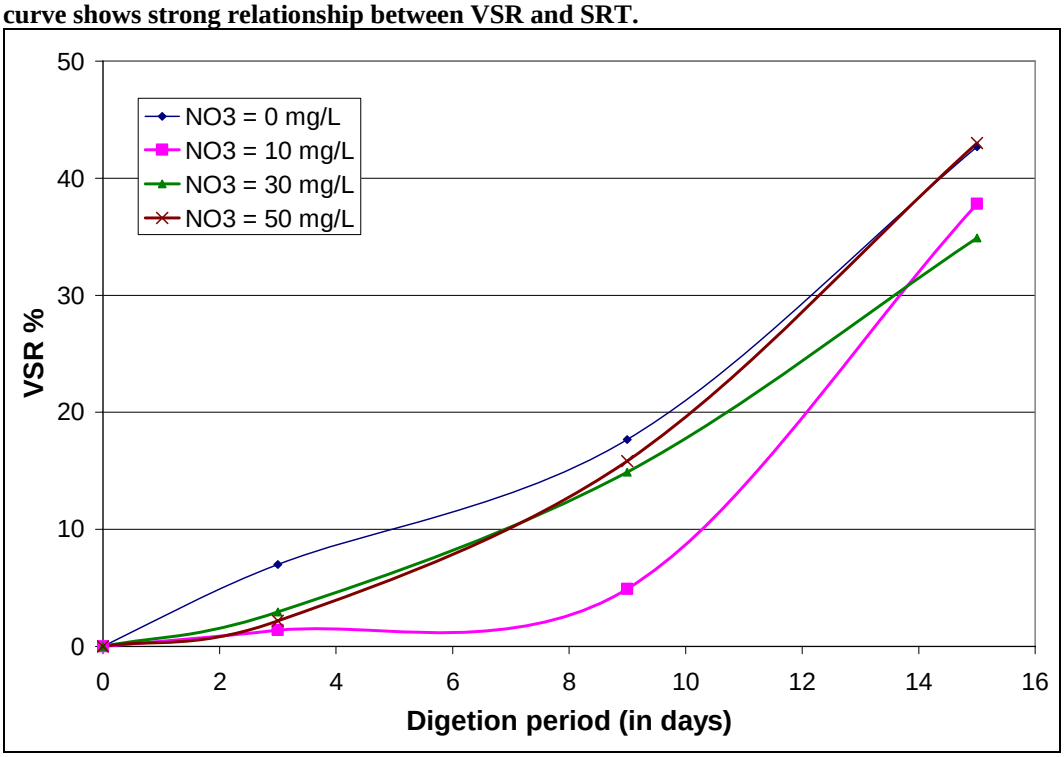

Figure A-10 – Nitrate spike effects volatile solids removal in negatively. Low VSR in high nitrate spiked digesters has been found.

Percent VSR as a function of the TKN removal was plotted to understand the effect of TKN removal on volatile solids. The correlation shows a strong relation between the two parameters for the nitrite spiked sludges. No linear correlation has been found in the un-spiked digester. Figure A-11 suggests that higher TKN removal occurs during the initial phase of VS reduction; i.e. when volatile solid reduction is less than 20 %. As more volatile solids are consumed, less TKN is removed from the solution. A plot of percent TKN removed and % VSR in nitrite spiked aerobic digestion suggests that a 10 mg/L nitrite spike is the optimum nitrite concentration at which maximum TKN removal can be achieved at the same VSR.

No linear correlation was found between % TKN removal and VSR for nitrate spiked aerobic systems. While for nitrite spiked samples, at lower VSR values it was observed that higher nitrite concentrations leads to removal of higher TKN, and at higher VSR the difference between the TKN removal percentages is small. This suggests that there nitrite may be playing an important role in TKN removal during the initial phase of digestion when VSR was less.

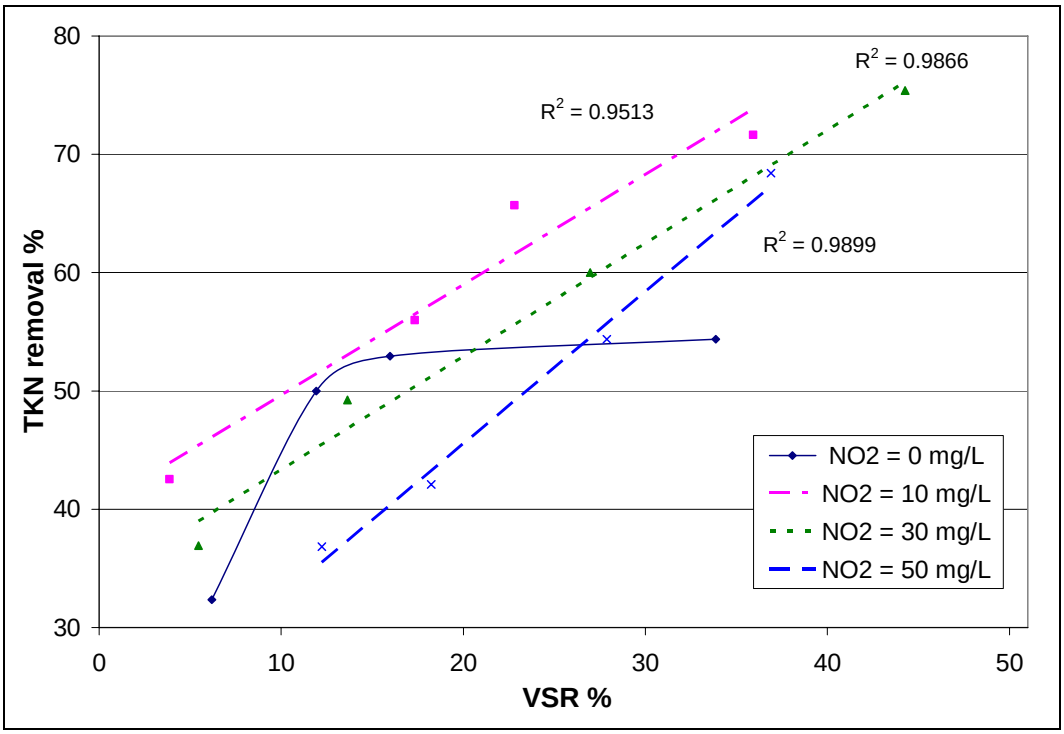

Figure A-11 – Strong correlation between percentage volatile solid removal and percentage of TKN removed during aerobic digestion exists. For no nitrite spike no linear correlation exits.

A.4 Conclusions

The aerobic digestion of anaerobic sludge spiked independently by nitrite or nitrate suggests that simultaneous nitrification and denitrification can take place during the initial phase of the digestion process. In the later phases of aerobic digestion nitrification became takes over the denitrification. Absence of both nitrate and nitrite, strong correlation between the ammonium loss and volatile fatty acid loss and high removal rates of both species during the initial phase of the operation supports that denitrification can take place during the aerobic digestion of anaerobic effluent.

It was found that nitrite spike enhance the ammonium, TKN and volatile solids removal from the aerobic digesters, while any appreciable difference was not found in the aerobic digesters spiked with nitrate. In addition it can be concluded that volatile fatty acid serve as a preferred carbon source for denitrification during aerobic phase of sequential anaerobic-aerobic digestion.

A.5 References

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Appendix B

Engineering Significance

The study of sequential anaerobic-aerobic digestion process helped to understand the advantages of the combined process over individual anaerobic and aerobic digestion processes. The combined process creates the opportunity to optimize the overall process on the bases of digestion process SRTs and temperature. Optimized selection of anaerobic and aerobic SRTs may help in simultaneous carbon-nitrogen load from the biosolids and may help in saving the operation cost. For example, it was observed during the investigation that percentage increase in VSR removal due to increase in 5 day SRT of anaerobic digestion was lesser than the corresponding increase in VSR upon increase in aerobic digestion SRT. This implies that for additional VSR less volume is required which implies cost saving in the operation. Additional cost saving will be due to –

1. Reduction in nitrogen loads in recycle streams, and
2. Improvement in dewatering and lesser polymer dose requirements.

Another advantage of presence of aerobic digestion after the anaerobic digester is that it may help saving the total digestion upset if anaerobic digesters perform poor. The later stage of aerobic digestion may act as shock absorbing unit due to the presence of more versatile and diverse heterotrophic bacteria in the system.

The sequential anaerobic-aerobic digestion process also show the ability for the sustainable development and some cost recovery options because of the quality of resulting biosolids. It was observed that odors in the resulting biosolids is almost 50% less than the conventional anaerobic biosolids and the nitrogen and carbon loading is in the appropriate range for the land applications. In addition, if digestion is carried out at thermophilic temperatures the solids will be able to meet class-A classification requirements and hence will be available for land application as fertilizer. If marketed appropriately, this will help in recovering back the investment made in

operation of the digestion process. Even if there is not favorable market for the biosolids, they will be more acceptable for land application because of the less odor production potential and lesser nutrient loads; and still saving money by providing more options for biosolids usage in comparison to only option of land fill.