Wastewater Carbon Diversion and Recovery via Primary Sludge Production, Thermal Hydrolysis, and Anaerobic Digestion

Hao Luo

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Zhi-Wu (Drew) Wang, Chair

Dietrich, Andrea M

Novak, John T

Nguyen, Caroline

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Wastewater Carbon Diversion and Recovery via Primary Sludge Production, Thermal Hydrolysis, and Anaerobic Digestion

Hao Luo

Abstract (academic)

This study is aimed to provide the latest understanding of cutting-edge technologies that enable wastewater organic carbon diversion and recovery through the enhancement of sludge production and blending, digestibility, dewaterability, and dewatered cake odor emission control. A comprehensive literature review showed that iron-based coagulants tend to show less negative impact than aluminum-based coagulants. This can be attributed to the reduction of ferric to ferrous ions in the course of anaerobic digestion (AD), which leads to a suite of changes in protein bioavailability, alkalinity and hydrogen sulfide levels, and in turn the sludge dewaterability and odor potential. In terms of the roles of thermal hydrolysis pretreatment (THP), the mechanism review indicated that the improvement of sludge dewaterability and anaerobic digestibility as a result of THP was because of the destruction of extracellular polymeric substances and increase of hydrolysis rate. However, THP also brings side effects such as high free residual ammonia and recalcitrant dissolved organic nitrogen (rDON) in the effluent. Besides, a comprehensive understanding of the formation of the odorous compounds in the sludge treatment processes indicated that sulfurous and nitrogenous compounds are usually regarded as the major odor-causing substances. Pilot THP-AD study indicated that adding aluminum to produce primary sludge can improve overall plant sludge digestibility, dewaterability, and well as the rDON reduction. Moreover, results from a pilot THP-AD and biochemical methane potential (BMP) test study indicated that adding a secondary thermal hydrolysis after a primary thermal hydrolysis-AD system can still create new BMP. Finally, a pilot study was conducted to evaluate the effect of aeration in the sludge holding tank on biosolids odor emission. The two rounds of bench-scale aeration studies indicated that aerating the sludge in holding tanks reduced peak emission concentrations of sulfurous odorous compounds. Further full-scale validation confirmed that aeration can be used by utilities as a simple means for biosolids odor control.

Wastewater Carbon Diversion and Recovery via Primary Sludge Production, Thermal Hydrolysis, and Anaerobic Digestion

Hao Luo

Abstract (general audience)

Public wastewater treatment annually consumed 3-4% energy production and contributed 1% greenhouse gas emission in the U.S. Meanwhile, the chemical energy contained in wastewater was estimated to be 9.3 times the energy it takes to treat it. Therefore, harvesting wastewater energy is proposed as a viable means for achieving energy and carbon neutral wastewater treatment. The approach to sending wastewater energy as much as possible to anaerobic digesters in which microorganisms help harvest useful energy in the form of flammable methane was evaluated in this study. From literature, we learned that chemicals used for upstream wastewater energy capture may make the downstream energy recovery difficult. While, thermal hydrolysis pretreatment, an industrial-scale pressure cooker, can be used to improve the ease of microbial bioenergy harvesting by making organics more biodegradable. However, thermal hydrolysis may also bring side effect in terms of recalcitrant organic formation. Also, in the course of energy recovery, the production and emission of nuisance odor may occur but can be controlled. Building on this existing knowledge, this study evaluated the pros and cons of the approach to using chemicals to capture and recover energy from wastewater. The results showed that the extents of energy recovery and savings was greater than the compromised solids reduction from the process. Moreover, results from a biochemical methane potential test study indicated that adding a secondary thermal hydrolysis can recover even more chemical energy from wastewater. In the end, a pilot study was conducted to develop a simple and economical approach to mitigating the odor emission issue during sludge handling. Results showed that pumping air into the sludge holding tank can substantially reduce peak odor emission. This approach was later verified in a full-scale test and recommended to utilities as a simple means for biosolids odor control.

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Publication List

Journal Papers

1. **Luo H.**, Zhang D., Taylor M., Nguyen C., Wang Z.W. (2021) Aeration in sludge holding tanks as an economical means for biosolids odor control – A case study, Water Environment Research, 2021;00:1–11, DOI: https://doi.org/10.1002/wer.1582
2. **Luo H.**, Sun Y., Taylor M., Nguyen C., Strawn M., Broderick T., Wang Z.W. (2021) Impacts of aluminum- and iron-based coagulants on municipal sludge anaerobic digestibility, dewaterability, and odor emission, Water Environment Research, 94(1), w1684, DOI: https://doi.org/10.1002/wer.1684
3. **Luo H.**, Wang Z.W., Wan C.X., Li Y.B. (2022), Thermal hydrolysis for enhanced anaerobic digestion, Progress in Energy and Combustion Science. (Submitted)
4. **Luo H.**, Taylor, M., Nguyen C., Wang Z.W. (2023), An experimental examination of carbon diversion to primary sludge: pros and cons (manuscript prepared)
5. **Luo H.,** Fasil H., Wang Z.W. (2023), Understanding the effect of a secondary thermal hydrolysis on municipal sludge anaerobic digestion (manuscript prepared)
6. Sun Y.P., **Luo H.**, Iboleon R., Wang Z.W. (2022) Fate of antibiotic resistance genes and class 1 integrons during sludge treatment using pilot-scale anaerobic digestion with thermal hydrolysis pretreatment, Bioresource Technology, 364(2): 128043, DOI: https://doi.org/10.1016/j.biortech.2022.128043

Book Chapter

7. **Luo H**., Sun Y., Yun Y., Wang Z.W. (2022) Odor generation, identification, and control during anaerobic digestion of biosolids. 2022;07:139-165. DOI: https://doi.org/10.1016/bs.aibe.2022.04.002

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8. **Luo H.**, Taylor M., Nguyen C., Quansah S., Wang Z.W. (2020) Identification of the Source, Cause, and Solution of the Biosolids Odor Emission in Western Branch Water Resource Recovery Facility, WEF Residuals and Biosolids 2020, Minneapolis, MN, March 31 – April 3 (Accepted but not presented due to COVID-19)
9. **Luo H.**, Taylor M., Nguyen C., Quansah S., Wang Z.W. (2020) Identification of the Source, Cause, and Solution of the Biosolids Odor Emission in Western Branch Water Resource Recovery Facility, ASABE 2020, Chicago, IL, July 12-15 (Accepted but not presented due to

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11. **Luo H.**, Taylor M., Nguyen C., Quansah S., Wang Z.W. (2020) Aeration of Sludge Holding Tanks Can Reduce Odor Emission from Dewatered Biosolids, WEFTEC 2020, New Orleans, LA, October 12-15 (Accepted but not presented due to COVID-19)
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13. **Luo H.**, Taylor M., Nguyen C., Quansah S., Wang Z.W. (2021) Identifying the Source, Cause, and Solutions for Biosolids Odor Control at a Maryland Water Resource Recovery Facility, WEF Residuals and Biosolids 2021, virtual, May 11-13
14. **Luo H.,** Hentz L., Wang Z.W. (2022) Effects of total solids contents, solids retention times, and primary/wasted sludge blending on the digestibility of thermal hydrolyzed municipal sludge, WEF Residuals and Biosolids 2022, Columbus, OH, May 24-27
15. **Luo H.,** Taylor M., Nguyen C., Wang Z.W. (2022) Effect of primary sludge and waste activated sludge blending on rDON formation in THP, AEESP 2022, St. Louis, MO, June 28-30
16. **Luo H.,** Taylor M., Nguyen C., Quansah S., Wang Z.W. (2022) Biosolids odor control through sludge holding tank aeration, ASABE 2022, Houston, TX, July 17-20
17. **Luo H.,** Haile F., Strawn M., Racey L, Wang Z.W. (2023) Does adding a secondary hydrolysis improve municipal sludge anaerobic digestion? WEF Residuals & Biosolids Conference 2023, May 16-19, Charlotte, NC

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18. Luo H., Freed C., Gillaspy G., Wang Z.W. (2021) Phosphorus immobilization in biochar produced from plants genetically engineered for luxury phosphorus uptake, WaterJam 2021, Virginia Beach, VA, September 13-16
19. **Luo H.**, Taylor M., Nguyen C., Keith T., Wang Z.W. (2022) Effect of oxidation reduction potential in the sludge holding tanks on odor emission from dewatered biosolids. 2022 AEESP Conference, June 28-30, St. Louis, MO

20. **Luo H.**, Taylor M., Nguyen C., Quansah S., Wang Z.W. (2020) Aeration of sludge holding tanks as an economical means for biosolids odor control, WaterJam 2020, Virtual, September 9-12
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Technical reports:

22. **Luo H.,** Zhang D., and Wang Z.W. (2020) Identification of the Source, Cause, and Solution of the Biosolids Odor Emission in Western Branch Water Resource Recovery Facility. Submitted to Washington Suburban Sanitary Commission, Mar 4
23. **Luo H.,** and Wang Z.W. (2020) Turning phosphorus pollution from digested dairy manure into a marketable product by using fungi. Submitted to Virginia Department of Agriculture and Consumer Services, Mar 15
24. **Luo H.,** and Wang Z.W. (2022) Effect of solids retention times on the performance of thermal hydrolysis pretreated mesophilic anaerobic digestion system. Submitted to Arlington County Water Pollution Control Plant, Sep 3
25. **Luo H.,** and Wang Z.W. (2022) Effects of primary sludge blending and aluminum addition on anaerobic digestion of alum-laden waste activated sludge. Submitted to Washington Suburban Sanitary Commission, Nov 1

Table of Contents

List of Figures

List of Tables

Chapter 1 Introduction

1.1 Background

Public wastewater treatment annually consumed 3-4 % energy production and contributed 1 % greenhouse gas emission in the U.S. (EPA, 2022; EPA, 2013). Meanwhile, the chemical energy contained in wastewater was estimated to be 9.3 times the energy it takes to treat it (Shizas and Bagley, 2004). Therefore, harvesting wastewater energy has been proposed as a viable means for achieving energy neutral wastewater treatment. Redirecting wastewater organic carbon as much as possible to anaerobic digester (AD) through primary sludge (PS) production in lieu of aeration tanks has been pursued as a pioneer approach for energy recovery and savings in water resource recovery facilities (WRRFs) (Guven et al., 2019; Nizami et al., 2017). This concept is opposite to the design of many existing WRRFs built during the first half of the 1900s when the primary focus was on water quality rather than energy management (Schmidt Jr and Dhulashia, 2020). As a consequence, many of these WRRFs are not even equipped with primary clarifiers and/or ADs. Minimizing total biosolids production through wastewater carbon oxidization to CO_2 in aeration tank has been a common design, making aeration tanks in WRRFs a major contributor to energy consumption and greenhouse gas emission (Guven et al., 2019). That being said, redirecting influent organic carbon to PS not only hold promise to increase energy recovery in ADs but also decrease electrical energy requirement for aeration, and in turn expanded WRRF capacity by reducing the organic loading upstream of the secondary process (Shewa et al., 2020).

Various primary treatment technologies have been implemented for PS production, including chemically or biologically enhanced sedimentation or mechanical screening and filtration, among which chemically enhanced primary treatment (CEPT) is the most popular as it achieves the greatest total suspended solids capture efficiency (e.g., 60-90%) (Schmidt Jr and Dhulashia, 2020), is easy and economical to implement, and remove phosphorus, dissolved heavy metal, as well as many other micropollutants at the same time (Shewa and Dagnew, 2020).

Although PS possesses much better biodegradability than wasted activated sludge (WAS), coagulants dosed into PS may play down the overall biodegradability of the two after blending (Luo et al., 2022). Moreover, diverting influent organics into PS is bound to increase the solids loading of ADs. In recent years, full-scale thermal hydrolysis pretreatment (THP) has been full-scale applied to improve the sludge digestibility and augment the capacity of existing ADs by increasing anaerobic digestion rates (Barber, 2016). However, THP also brings side effects, one of which is the formation of recalcitrant dissolved organic nitrogen (rDON) (Zhang et al., 2020b). It has been recognized that rDON formed during THP is mainly from the Maillard reaction between the carbonyl groups of reducing sugar and the amino groups of proteins (Zhang et al., 2021a; Zhang et al., 2020b). This is because the typical THP conditions, e.g., 165 °C for 30 min, overlap with that of the Maillard reaction. More importantly, PS and WAS are mainly composed of carbohydrates and proteins, which are the precursors of carbonyl groups and the amino groups, respectively. Therefore, blending PS with WAS as commonly practiced in WRRFs provides an ideal recipe for Maillard reaction and in turn rDON production in THP (Hodge et al., 1972). rDON is responsible for total nitrogen increase in the discharge, biological nitrogen removal inhibition, and UV transmission blockage (Abelleira-Pereira et al., 2015; Dwyer et al., 2008).

Anaerobic digestion of municipal sludge has been widely applied in water resource recovery facilities (WRRFs) as a sustainable approach with many advantages such as solids reduction and bioenergy recovery (Zamri et al., 2021). However, this conventional technology can be affected by various sludge treatment processes such as upstream chemical coagulation and thermal hydrolysis pretreatment (THP). Besides, the unpleasant smell of odorous compounds produced as the by-product of the anaerobic fermentation of dewatered biosolids has been raised as a major concern in WRRFs (Novak et al., 2006). Therefore, it is necessary to understand the effects of these sludge pretreatments on sludge anaerobic digestion as well as the dewatered cake biosolids odor emission.

First of all, the objective of this research is to experimentally examine the pros and cons of CEPT-enabled carbon diversion to PS in terms of overall energy recovery, solids reduction, as well as dissolved compound removal. To this end, three scenarios were compared in parallel, i.e., (i) WAS only without PS production; (ii) PS production to 1:1 dry mass ratio with WAS; and (iii) PS

production to 3:1 dry mass ratio with WAS. Additional control experiments were also added to assist the understanding of mechanisms. THP was adopted in all three scenarios to reflect the state-of-the-art of the sewage sludge anaerobic digestion enhancement. The pros and cons of each scenario were analyzed. It is the intention of this study to inform the wastewater industry of not only the benefits but also the hidden pitfalls of carbon diversion with first-hand experimental data.

Second, aluminum-and iron-based chemicals have been broadly used as the two most common types of coagulants for wastewater treatment (Sahu and Chaudhari, 2013). However, the impacts of these two inorganic coagulants on the performance of downstream sludge management can be quite different and have not been well understood. It has been reported from previous studies that that aluminum/iron addition could affect the anaerobic digestibility, dewatering of sludge and odor emission from biosolids (Novak and Park, 2010a; Ojo and Ifelebuegu, 2019). Therefore, the first object of this dissertation is to focus on the effects of aluminum-/iron-based coagulants on the sludge handling process and provide guidance for selecting the appropriate coagulants according to the physiochemical properties of the target sludge.

Third, THP of sewage sludge is widely applied in the full-scale WRRFs for intensifying the treatment capacities of ADs by applying high temperature and pressure (160 -180 ºC) to the sludge prior to anaerobic digestion (Barber, 2016). THP was reported to have numerous advantages in terms of sewage sludge pretreatment such as improving sludge dewaterability and increasing rates of anaerobic digestion and biogas production (Higgins et al., 2011). The SRTs of AD fed with THP pretreated sewage sludge can be shortened from 25-30 days to 10-15 days (Barber, 2016). However, some disadvantages was also reported such as free ammonia production and recalcitrant dissolved compounds formation (Zhang et al., 2020b). Therefore, the second objective of this dissertation is to understand the mechanisms of THP and its effects on AD.

Forth, the anaerobic biological reactions occurring in the WRRFs during the sludge handling processes break down sulfurous and nitrogenous substances such as urea, proteins, and amino acids, which are precursors of sulfurous and nitrogenous odorous compounds (Ren et al., 2019). Once formed, these odorous compounds could be released to the atmosphere in the course of the sludge dewatering, storage, and land application. These unpleasant smell can lead to the deterioration in

the quality of life and depreciation of the real estate values in the neighboring communities (Gostelow et al., 2001). Therefore, the fourth part of this dissertation is to understand the formation of these odorous compounds and the odor control strategies.

In short, this dissertation is aimed to provide the latest understanding of the cutting-edge technologies that enable wastewater organic carbon diversion and recovery through the enhancement of sludge production, blending, digestibility, dewaterability, and dewatered cake odor emission control.

1.2 Outline

This dissertation has 7 chapters in total. At the beginning of this dissertation, three literature reviews were conducted to earn a state-of-the-art understanding of the current challenges in municipal sludge management with regard to the sludge blending, digestibility, dewaterability, and odor emission, as well as the potential cost-effective countermeasures available to address these challenges. Briefly, **Chapter 2** investigated the impacts of aluminum- and iron-based coagulants on the sludge anaerobic digestibility, dewaterability, and odor emission. Results showed that the iron-based coagulants tend to show less negative impact than aluminum-based coagulants mainly due to the reduction of ferric to ferrous ions in the course of anaerobic digestion, which leads to a suite of changes in protein bioavailability, alkalinity and H_2S levels, and in turn the sludge dewaterability as well as the odor potential. **Chapter 3** reviewed the previous published works related to the roles of THP in municipal sludge management. Then, a comprehensive review of the mechanisms responsible for odor generation, identification, and control during anaerobic digestion of municipal sludge was summarized in **Chapter 4** for development of solutions to this unpleasant smell issue. Following the literature review, the effect of sludge blending and aluminum addition on THP-enhanced AD system and recalcitrant dissolved nitrogen formation was evaluated in **Chapter 5.** It has been found out that adding a PS clarifier to produce PS via chemical enhanced primary treatment can improve the overall plant sludge digestibility and dewaterability. Moreover, the effect of a secondary thermal hydrolysis on municipal sludge anaerobic digestibility was also tested in **Chapter 6**. Results indicated that adding a secondary thermal hydrolysis after a primary thermal hydrolysis-AD system can still create new biological methane potential. In the end,

Chapter 7 introduced an economical strategy for dewatered biosolids odor control through the aeration of the sludge holding tanks. The results showed that continuous aeration in the sludge holding tanks could lift oxidation reduction potential of the sludge from -180 mV to -120 mV over 64-hour storage time, which in turn reduces the odor emission from dewatered biosolids. The new knowledge created in this dissertation is anticipated to provide mechanistic guidance for industrial implementation of practical design for achieving energy neutrality and improved municipal sludge management.

1.3 Attribution

Each coauthor is duly credited for his or her contribution to this work, both in their sharing of ideas and technical expertise.

Zhi-Wu (Drew) Wang, Ph.D., Assistant Professor
Department of Biological System Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061

Co-authors of Chapters 2, 3, 4, 5, 6, 7

Dian Zhang, Engineer
Stantec, Washington DC, 20005

Coauthor of Chapter 7

Mary Strawn, Chief Engineer
Arlington County Water Pollution Control Bureau, Arlington, VA 22201

Coauthor of Chapter 2, 6

Yuepeng Sun, Postdoctor
Department of Civil and Environmental Engineering, George Washington University, Washington DC, 20052

Coauthor of Chapter 2, 4

Caroline Nguyen, Principal Scientist
WSSC Water, Laurel, MD, 20723

Coauthor of Chapters 2, 5, 7

Malcolm Taylor, Principal Environmental Engineer
WSSC Water, Laurel, MD, 20723

Coauthor of Chapters 2, 5, 7

Tom Broderick, Project Manager
Arlington County Water Pollution Control Bureau, Arlington, VA 22201

Coauthor of Chapter 2

Yun Yin, Ph.D., Assistant Professor
Department of Food Science and Technology, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061

Coauthor of Chapter 4

Fasil Haile, Project Engineer
Arlington County Water Pollution Control Bureau, Arlington, VA 22201

Coauthor of Chapter 6

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Chapter 2 Impacts of aluminum- and iron-based coagulants on municipal sludge anaerobic digestibility, dewaterability, and odor emission

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2.1 Abstract

Although aluminum- and iron-based chemicals have been broadly used as the two most common types of coagulants for wastewater treatment, their impacts on the performance of downstream sludge management can be quite different and have not been well understood. This work reviewed and analyzed their similarities and differences in the context of the anaerobic digestion performance, dewaterability of digested sludge, and odor emission from dewatered biosolids. In short, iron-based coagulants tend to show less negative impact than aluminum-based coagulants. This can be attributed to the reduction of ferric to ferrous ions in the course of anaerobic digestion, which leads to a suite of changes in protein bioavailability, alkalinity and hydrogen sulfide levels, and in turn the sludge dewaterability and odor potential. Whether these observations still hold true in the context of thermally hydrolyzed sludge management remains to be studied.

2.2 Keywords

Activated sludge; Aluminum; Anaerobic digestion; Coagulation; Dewaterability; Iron

2.3 Introduction

Chemical coagulation through the addition of inorganic salts of multivalent metals is one of the essential processes for the separation of liquid from solids (e.g., colloids) for pollutant removal (e.g., organic matters and phosphorus) in water and wastewater (Pernitsky and Edzwald, 2006). The basic mechanisms include surface adsorption, charge neutralization, interparticle bridging, and floc sweeping (Metcalf et al., 2014). Briefly, the negatively charged colloidal particles in the water are destabilized after diminishing their surface charge by the adsorption of metal cations. The coagulants can adsorb colloidal particles and form a bridge. Additionally, precipitates of metal hydroxides enmeshed with colloidal particles can form when sufficient metal salt is added (Metcalf et al., 2014). Coagulation is therefore an effective method aiding wastewater treatment and has been used for treating various types of wastewaters including municipal sewage, palm oil mill effluent, textile wastewater, pulp mill wastewater, oily wastewater, sanitary landfill leachates, and others (Lee et al., 2014).

Common coagulant choices in the water resource recovery facilities (WRRFs) are aluminum-based coagulants mainly including aluminum sulfate ($Al_2(SO_4)_3$), polyaluminum chloride (PAC), composite PAC, and iron-based coagulants mainly including ferric sulfate ($Fe_2(SO_4)_3$), ferric chloride ($FeCl_3$), and ferrous sulfate ($FeSO_4$) for their cost-effectiveness (Sahu and Chaudhari, 2013; Shewa and Dagnew, 2020). These coagulants can also be used for the removal of phosphorus (Szabó et al., 2008; Takács et al., 2006). The optimal pH for the aluminum sulfate is in the range of 5 to 8, while ferric is more efficient than alum for phosphorus removal only at acidic pH values below 6 (Maher et al., 2015). The optimum doses of aluminum/iron-based coagulants in wastewater range from 12 to 13000 mg L^{-1} and depends on the types of wastewater and coagulants used, as well as the target contaminants and their removal levels (Shewa and Dagnew, 2020).

The application of aluminum/iron-based coagulants in wastewater treatment, however, has drawbacks. Overdosing would increase the metal concentration in the effluent, which may have adverse impact on aquatic organisms (Rostern, 2017). Inorganic salts can lead to a 37% – 97% increase of sludge volume (Yeoman et al., 1988) and reduced anaerobic biodegradability (Shewa

and Dagnew, 2020), which may challenge the downstream sludge management processes such as anaerobic digestion and sludge dewatering (Gossett et al., 1978).

Previous studies revealed that aluminum/iron addition affected the digestibility and dewatering of sludge, and odor emission from biosolids (Gossett et al., 1978; Novak and Park, 2010b; Ojo and Ifelebuegu, 2019). It is necessary to review the effects of aluminum/iron-based coagulants on the sludge handling process and provide guidance for selecting the appropriate coagulants according to the physiochemical properties of the target sludge. We aim to understand the interaction between aluminum/iron-based coagulants and activated sludge as well as the impacts of coagulant addition on the performance of anaerobic digestion, dewaterability of sludge, and odor emission from dewatered biosolids. Fundamental understanding of the interaction between aluminum/iron-based coagulants and activated sludge.

2.4 Fundamental understanding of the interaction between aluminum/iron-based coagulants and activated sludge

Extracellular polymeric substances (EPSs) are predominant constituents of activated sludge and account for 60 – 80% of the total biomass (Liu and Fang, 2003). It plays important roles in the removal of pollutants from wastewater in the course of sludge bioflocculation and dewatering (Flemming et al., 2000; Wingernder et al., 1999). Proteins and polysaccharides are dominant components in both loosely bound EPSs (LB-EPSs) and tightly bound EPSs (TB-EPSs). The interaction between inorganic coagulants and components of EPSs was regarded as the major mechanism facilitating sludge dewatering performance (Niu et al., 2013). Metal cations can bind proteins or polysaccharides of both LB-EPSs and TB-EPSs during the coagulation and thus may influence the EPSs composition and regulate the sludge dewatering (Higgins and Novak, 1997). The sludge dewaterability performance was found to be much more closely correlated to the contents of LB-EPSs than TB-EPSs (Li and Yang, 2007).

Oxidized form of iron (e.g. Fe^{3+}) must have played an essential role in binding and stabilizing the activated sludge structure because iron cation reduction has been shown to increase the turbidity of activated sludge mixed liquor (Caccavo et al., 1996; Nielsen and Keiding, 1998). The interaction

between EPSs and iron cations (e.g. Fe^{3+}) are known to be involved in sludge flocculation (Nielsen and Keiding, 1998) because iron cations have high affinity for the protein fraction of the sludge EPSs (Murthy and Novak, 1999). As a matter of fact, both Al^{3+} and Fe^{3+} neutralizes the negative charge of the EPSs by selectively binding functional groups such as -OH, N-H, C=O, and C-N in EPSs (Liu et al., 2018; Sayre et al., 2010; Suganya et al., 2017; Sugishima et al., 2007). It is noteworthy that proteins contain all these four functional groups, while polysaccharides only contain -OH and C=O. Hence, it is not surprising to see that the affinity of aluminum/iron-based coagulants to proteins is higher than that to the polysaccharides (Murthy et al., 2000; Vilgé-Ritter et al., 1999). The aluminum cations can interact with amino acids such as Aspartate, Serine, Threonine, and Tyrosine and induce the shifts of their pK_a values (Mujika et al., 2014). Usually, secondary sludge contains greater protein content, e.g., 32-41 % of total solids, than primary sludge, e.g., 20-30 % of total solids (Tezel et al., 2011). Therefore, the aluminum/iron-based coagulants are expected to play greater binding effects on secondary sludge than primary sludge in the sludge treatment trains.

2.5 Aluminum/iron-based coagulants impact the sludge digestibility

The impacts of aluminum/iron-based coagulant addition on sludge digestibility are reviewed and summarized in Table 2.1. In general, aluminum-based coagulants were reported to have adverse effects on anaerobic digester performance; yet, contradictory results have been reported for the effects of iron-based coagulants.

Table 2.1. The impact of iron/aluminum-based coagulants on biogas/methane production, VFAs, and VSR.

Coagulant	Coagulant dose*	VSR	VFAs	Biogas/Methane	H_2S change (%)	References
$Al_2(SO_4)_3$	0.2 – 1.5 %	2% (↓)				(Novak and Park, 2010b)
$Al_2(SO_4)_3$	32 – 63 mg L^{-1}	9% - 29% (↓)	25% - 325% (↑)	3% - 16% (↓) (CH_4) 7% - 17% (↓) (biogas)		(Gossett et al., 1978)
$Al_2(SO_4)_3$	1.0 %	6.8% (↓)	600% (↑)		311 % (↑)	(Abbott & Eskicioglu, 2015)
$Al_2(SO_4)_3$	100 mg L^{-1}			21% (↓)		(Ojo and Ifelebuegu, 2019)
$Al_2(SO_4)_3$	108 mg L^{-1}			30% (↓) (CH_4)		(Kindzierski and Hrudey, 1986)
$Al_2(SO_4)_3$	16.2 – 32.4 mg L^{-1}			22% - 29% (↓) (biogas)		(Dentel and Gossett, 1982)
$Al_2(SO_4)_3$	10 mg L^{-1}				850 % (↑)	(Parker et al., 2020)
PAC	120 mg L^{-1}		93% (↓)	10% (↓) (CH_4)		(Kim and Chung, 2015)
PAC	16 -24 mg L^{-1}		35% (↓)			(Kim and Chung, 2015)
$FeCl_3$	5650 mg L^{-1}	No effect		5% (↓) (CH_4)		(Jackson-Moss and Duncan, 1990)
$FeCl_3$	0.2 – 1.2 %	No effect				(Novak and Park, 2010b)
$FeCl_3$/PAC	0.05 %	No effect		No effect (CH_4)		(Akgul et al., 2017)

$FeCl_3$	762 – 2900 mg L^{-1}	2% - 6% (↑)	38-54% (↑) (CH_4) 28-40% (↑) (biogas)		(Ju et al., 2016)
$FeCl_3$	0.7 %	6.2% (↓)		78 % (↓)	(Abbott & Eskicioglu, 2015)
$FeCl_3$	46 mg L^{-1}46 mg L^{-1}		10% (↓) (CH_4)		(Kim and Chung, 2015)
$FeCl_3$	100 mg L^{-1}100 mg L^{-1}		36% (↓)		(Ojo and Ifelebuegu, 2019)
$FeCl_3$	232 mg L^{-1}232 mg L^{-1}		30% (↓)		(Kim and Chung, 2015)
$FeCl_3$	364 mg L^{-1}		20% (↓) (CH_4)		(Kindzierski and Hrudey, 1986)
$FeCl_3$	34.4 - 86 mg L^{-1}		21% - 32% (↓) (biogas)		(Dentel and Gossett, 1982)
$FeSO_4$	1.84 mg Fe^{2+} / mg^{-1} phosphorus			100 % (↓) when switch from $Al_2(SO_4)_3$ to $FeSO_4$	(Parker et al., 2020)
$FeCl_3$	1.25 %			Almost 100 % (↓)	(Park and Novak, 2013)
$FeCl_3$	10 mg L^{-1}			77 % (↓)	(Abbott, 2014)

* Percentage values are showed as Al^{3+} or Fe^{3+} g g^{-1} dry solids; Up and down arrows indicate the decrease and increase effect, respectively.

2.5.1 Effects of aluminum-based coagulants

Methane production in anaerobic digestion involves four steps, i.e., hydrolysis, acidogenesis, acetogenesis, and methanogenesis. As shown in Table 2.1, aluminum-based coagulants impacted the volatile solids reduction (VSR) and the production of intermediate as well as the final products such as volatile fatty acids (VFAs) and methane. VSR depends on the hydrolysis efficiency which is the first step of anaerobic digestion and relies on bacterial hydrolytic enzymes to break down volatile solids. Generally, adding aluminum-based coagulants decreased VSR during anaerobic digestion (Gossett et al. 1978; Abbott & Eskicioglu 2015; Novak & Park 2010). For example, 9 – 29% less VSR was observed when the aluminum cation concentration was 32 – 63 mg Al^{3+} L^{-1} (Gossett et al., 1978). VFAs include acetic, propionic, iso-butyric, n-butyric, iso-valeric and n-valeric acids (Xu et al., 2017) and are intermediate products from acidogenesis. Adding $AlCl_3$-based coagulants was found to decrease the VFAs production during anaerobic digestion probably because the wrapping of sludge particles by Al^{3+} has decreased the hydrolysis rate (Kim and Chung, 2015; Lin et al., 2017). For example, PAC with dose exceeding 232 mg Al^{3+} L^{-1} decreased 93% of the conversion efficiency of organic substrates to VFAs (Kim and Chung, 2015). Similarly, 8 – 35% reduction of VFAs production was observed in the PAC-treated sludge with dose of 16 – 24 mg Al^{3+} L^{-1} (Lin et al., 2017). In the opposite, adding alum-based coagulants was found to increase the VFAs production probably because of the hydrogen sulfide (H_2S) production which has inhibited VFA utilization by methanogens (Abbott and Eskicioglu, 2015; Gossett et al., 1978).

The influence of aluminum-based coagulant addition on methane production has also been documented in literature (Table 2.1). It has been reported that a 3–30% decrease of methane production was observed during the anaerobic digestion, depending on the aluminum concentrations in the feed sludge (Dentel and Gossett, 1982; Gossett et al., 1978; Kindzierski and Hrudey, 1986; Ojo and Ifelebuegu, 2019). Moreover, adding alum-based coagulants such as $Al_2(SO_4)_3$ into anaerobic digesters caused performance instability, biogas production cease, and reactor failure (Abbott and Eskicioglu, 2015). This was mainly attributed to VFA accumulation induced by the toxicity of H_2S formed from the reduction of $Al_2(SO_4)_3$ but not by the aluminum cations (Abbott and Eskicioglu, 2015). The effect of aluminum-based coagulant addition on the methane production, however, seems to depend on the duration of acclimation (Akgul et al., 2017;

Cabirol et al., 2003). Studies revealed that aluminum-based coagulant addition had minor impact on methane production in lab-scale semicontinuous anaerobic digesters under mesophilic condition after a long acclimation period, e.g., over 100 days (Akgul et al., 2017; Cabirol et al., 2003).

2.5.2 Mechanisms behind the effects of aluminum-based coagulants on the sludge digestibility

As summarized in Table 2.2, the adverse effects of aluminum-based coagulants on the anaerobic digester performance should not be attributed to the coagulant toxicity (Gossett et al., 1978; Kim and Chung, 2015). Instead, the envelopment of substrate by coagulants could have posed a barrier for hydrolytic enzymes to access the organic substrate (Kim and Chung, 2015; Lin et al., 2017). The hydrolysis rate constant (K_h) for sludge fermentation was found to decrease from 0.032 L day^{-1} for the sludge without PAC to 0.017 L day^{-1} for the sludge with a PAC dose of 24 mg Al^{3+} L^{-1} (Lin et al., 2017). Since hydrolysis is often considered the rate-limiting step of anaerobic digestion (Park et al., 2005), the reduced hydrolysis rate as a result of binding between aluminum cations and organic substrate in EPSs is expected to adversely affect sludge anaerobic digestibility.

The reduced hydrolysis rate in turn affects the digester alkalinity. Alkalinity is the buffering capacity of water to neutralize acids. Anaerobic digestion stability depends on the buffering capacity of the digester contents. Here, ammonia-associated alkalinity can play an important role in balancing the total alkalinity as ammonia-associated alkalinity can be 90% of the total alkalinity in the anaerobic digesters (Gossett et al., 1978). However, aluminum-based coagulants such as $Al_2(SO_4)_3$ can reduce the biodegradability of organic materials through protein binding. Organic nitrogen decomposition in chemical sludges with aluminum-based coagulant addition was found to decrease by 50% compared to the control sludge without aluminum-based coagulant addition (Gossett et al., 1978). The aluminum-based coagulant addition with the dose of 46 mg Al^{3+} L^{-1} reduced ammonia production of the anaerobic digesters from 600 to 230 mg NH_3-N L^{-1} (Metcalf et al., 1991). As a result, the total alkalinity decreased from 2600 to 1050 mg $CaCO_3$ L^{-1}, which is lower than the normal alkalinity range (2000 to 5000 mg L^{-1} as $CaCO_3$) in the anaerobic digesters

(Metcalf et al., 1979). Therefore, the aluminum-based coagulant addition could deteriorate the performance of anaerobic digesters by reducing pH-buffer capacity through alkalinity reduction.

Besides the negative effects on anaerobic hydrolysis rate and digester alkalinity, aluminum-based coagulant addition was also reported to affect the growth of anaerobic microorganisms. The conversion of inorganic sulfate into H_2S as the result of sulfate reduction hampered the growth of methanogens (Chen et al., 2008). Hence, both aluminum cation and sulfate anion addition inhibited the specific methanogenic activity of methanogenic and acetogenic bacteria, resulting in a 50% to 72% decrease of their activities in the anaerobic digestion of the sludge from enhanced primary treatment (Cabirol et al., 2003).

2.5.3 Effects of iron-based coagulants

Contradictory results have been reported for the effects of iron-based coagulants on anaerobic digester performance (Table 2.1). This is mainly because iron-based coagulants could express multiple cross-effects. In general, iron addition showed limited impacts on VSR in all literature in Table 2.1 except the studies by Ju et al. (2016) and Abbott and Eskicioglu (2015). Ju et al. (2016) reported that the addition of iron cations increased VSR, likely because the treated sludge (sulfate-rich saline chemically enhanced primary treatment sludge) contained high concentration of sulfide, which precipitated with Fe^{2+} reduced from Fe^{3+}, mitigating the inhibitory effect of the sulfide (Ju et al., 2016). On the other hand, the precipitation and bioavailability reduction of organic matters in association with iron cations also can play an adverse effect on VSR. Abbott and Eskicioglu (2015) reported that $FeCl_3$ addition resulted in 6.8% VSR decrease during the anaerobic digestion of municipal waste sludge with the dose of 10.74 mg Fe^{3+} g^{-1} dry solids (Abbott and Eskicioglu, 2015).

Table 2.2. Mechanisms of aluminum/iron-based coagulants in influencing sludge digestibility, dewaterability, and odor emission

	Effect on sludge anaerobic digestibility	Effect on sludge dewaterability and odor emission
Positive effects	• Reduction of Fe^{3+} to Fe^{2+} can release available protein for degradation • Sulfide precipitation with Fe^{2+}, mitigating the toxic effect of H_2S to the bacteria • Crucial role of iron as a growth factor of methanogens • Mitigating the high level of VFA accumulation by promoting acid utilization as a key trace element (Fe)	• Making EPSs structure more compressed • Removing water trapped in the EPSs • Acting as the skeleton builders to increase floc porosity • Reducing the bioavailability of odor precursors, such as protein • Sulfide precipitation with Fe^{2+}, reducing odor concentration
Negative effects	• Al^{3+} and Fe^{3+} may bind with protein fraction in EPSs, reducing protein bioavailability for anaerobic digestion • Formation of FeS on the surface of methanogenic cells could inhibit methanogenic activities • Iron reduction can outcompete methanogenesis • Sulfate contained in the alum can be easily converted into H_2S, creating toxic effect	• Sulfate contained in the alum can be easily converted into H_2S, increasing odor generation from the anaerobic digester

Contradictory results have also been reported for the effects of iron-based coagulant addition on VFAs and methane production during anaerobic digestion (Table 2.1). $FeCl_3$ at a dose exceeding 232 mg Fe^{3+} L^{-1} led to a 30% decrease in the conversion efficiency of organic substrates to VFAs in fermented synthetic chemically enhanced primary sludge under mesophilic conditions (Kim and Chung, 2015). Reduction of 10% – 36% methane or biogas production was observed with addition of $FeCl_3$ ranging from 34 to 364 mg L^{-1} (Dentel and Gossett, 1982; Kim and Chung, 2015; Kindzierski and Hrudey, 1986; Ojo and Ifelebuegu, 2019).

However, some studies have also shown that iron-based coagulants had minimal effects on sludge anaerobic digestibility. For example, iron cations at the dose of 5650 mg Fe^{3+} L^{-1} had limited inhibitory effects on anaerobic digestion with only a 5% biogas production decrease (Jackson-Moss and Duncan, 1990). The $FeCl_3$ addition at 0.05% g Fe^{3+} g^{-1} dry solids was reported to be well tolerated and did not impact methane production (Akgul et al., 2017). $FeCl_3$ dosed at 10 – 30 mg Fe^{3+} L^{-1} increased ~9% VFAs production in fermented chemically enhanced primary sludge under mesophilic conditions (Lin et al., 2017). Several studies even reported that iron-based coagulants can improve the methane production (Achouri et al., 2017; Ju et al., 2016).

2.5.4 Mechanisms behind the effects of iron-based coagulants on the sludge digestibility

Compared to aluminum-based coagulants, iron-based coagulants had less impacts on the sludge anaerobic digestibility or even had improvement on the sludge digestibility. This can be possibly explained by (1) reduction of Fe^{3+} to Fe^{2+}; (2) sulfide precipitation with Fe^{2+}; and (3) crucial role of iron for the growth of methanogens (Table 2.2).

Fe^{3+} can bind the protein fraction of EPSs so that the proteins may become unavailable for the microorganisms. However, Fe^{3+} reduction by iron reducing bacteria during the anaerobic digestion breaks the bond between protein and ferric ions, making the iron-associated organics more bioavailable (Park and Novak, 2013). The reduction of Fe^{3+} to Fe^{2+} can occur rapidly under anaerobic conditions. Because Fe^{2+} itself has high solubility, Fe^{3+} reduction can lead to the disintegration of sludge flocs and the releasing of organics such as protein into the solution

(Brezonik and Arnold, 2011). The Fe^{3+} reduction might couple with the oxidation of hydrogen or organic substrates such as benzoate as illustrated in Eqs. 1 and 2 (Baek et al., 2019). Iron-reducing bacteria, therefore, can participate in the decomposition of complex organic matter, enhancing sludge solubilization (Wang et al., 2018). On the other hand, Fe^{3+} reduction can outcompete other metabolic pathways, such as methanogenesis in certain environments, resulting the deterioration of the anaerobic digester performance. Thermodynamic evidence showed a higher standard reduction potential of Fe^{3+} to Fe^{2+} (-0.19 V) than that of CO_2 to CH_4 (-0.24 V) (Baek et al., 2019). The competitive inhibition of methanogenesis happens when the electron donor, e.g. H_2 and organics, for respiratory process is limited (Wang et al., 2018).

$$H_2 + 2Fe^{3+} \rightarrow H^+ + 2Fe^{2+} \quad (1)$$

$$Benzoate + 30Fe^{3+} + 19H_2O \rightarrow 7HCO^- + 30Fe^{2+} + 36H^+ \quad (2)$$

The formation of sulfide precipitates with Fe^{2+} may mitigate the inhibitory effect from H_2S produced during anaerobic digestion (Ge et al., 2013). H_2S is the toxic form of sulfide to the microorganisms (Chen et al., 2008). Sulfate reducing bacteria and methanogens enriched under the same conditions compete for organic substrates, causing the competitive inhibition of methanogenesis (Van Lier et al., 2008). Iron salt addition in anaerobic environment can effectively control inhibitive H_2S concentration of anaerobic digester through FeS precipitation (Dezham et al., 1988; Hauduc et al., 2019). On the other hand, the deposit of FeS on the surface of methanogenic cells has been reported to reduce enzymatic activities and reactant accessibility such as VFAs, which in turn inhibit methanogenic activities (Ge et al., 2013). This may explain the contradictory results for the effects of iron-based coagulant addition on anaerobic digestibility in the literature.

Iron is also one of the major trace elements for the growth of microorganisms such as methanogens (Choong et al., 2016). Sufficient level of trace elements such as iron can support the growth of methanogens and ensure the stable operation. Iron is also one of the major trace elements in the content of metalloenzymes for both acetogenesis and methanogenesis (Choong et al., 2016). $FeCl_3$ was reported to enrich Coprothermobacter for proteins fermentation and Methanosarcina for

methanogenesis (Yu et al., 2016). Thus, iron dosing could mitigate the inhibitory effect of high VFA accumulation and promote acid utilization for methane production (Yu et al., 2016).

2.6 Aluminum/iron-based coagulants impact the sludge dewaterability

Aluminum/iron-based salts are also used during sludge dewatering to achieve better solid capture. Many studies were performed to examine the effects of aluminum/iron-based coagulant addition on the sludge dewaterability with capillary suction time (CST) and specific resistance to filtration (SRF) as monitoring parameters. CST represents the time it takes for the water to be released from the sludge matrix, while SRF is the resistance of the filter cake to the transport of filtrate through the cake (Ng and Hermanowicz, 2005). Therefore, a reduction of CST or SRF reflects the sludge dewaterability improvement.

2.6.1 Effect of aluminum/iron-based coagulants on the sludge dewaterability

Overall, aluminum/iron-based coagulants improve the sludge dewaterability by decreasing the CST and SRF (Table 2.3). For instance, activated sludge conditioned with 0.2% g Fe^{3+} g^{-1} dry solids and 0.2% g Al^{3+} g^{-1} dry solids salts resulted in 41 % and 44 % CST reduction, respectively (Lau et al., 2013). Likewise, SRF (m kg^{-1}) was reduced from 1.7×10^{12} to 3.98×10^{11} (77% reduction) and 2.08×10^{11} (88% reduction) when PAC and composite PAC was dosed at 0.26% and 0.79% (g Al^{3+} g^{-1} dry solids), respectively (Zhang et al., 2014b). SRF was also reduced by 82% with $FeCl_3$ addition at the dose of 5% g Fe^{3+} g^{-1} dry solids (Jing et al., 1999).

Table 2.3. The impact of aluminum/iron-based coagulants on CST and SRF reduction

Coagulant	Coagulant Dose*	CST reduction	SRF reduction	References
$AlCl_3$	0.20%	41%		(Ju et al., 2016)
$Al_2(SO_4)_3$	2.1%	68 %		(Turchiuli and Fargues, 2004)
$Al_2(SO_4)_3$	0.1%		30 %	(Sun et al., 2015)
$Al_2(SO_4)_3$	0.01%	23%	36 %	(Barati Rashvanlou et al., 2020)
$Al_2(SO_4)_3$	3.2 %	72.96 %		(Ojo and Ifelebuegu, 2019)
PAC	0.26%		77%	(Zhang et al., 2014b)
Composite PAC	0.79%		88%	(Zhang et al., 2014b)
$FeCl_3$	5 %		82%	(Jing et al., 1999)
$FeCl_3$	23 %	71.4 %	93.8 %	(Liu et al., 2012a)
$FeCl_3$	3.2 %	63.82 %		(Amarasekara and Deng, 2019)
$FeCl_3$	0.2%	44%		(Ju et al., 2016)

*as Al^{3+} or Fe^{3+} g g^{-1} dry solids

2.6.2 Mechanisms behind the effects of aluminum/iron-based coagulants on the sludge digestibility

EPSs play an important role in sludge dewatering. The improvement of sludge dewaterability with aluminum/iron-based coagulant conditioning can be explained by the interaction between coagulants and EPSs. First, EPSs were believed to be compressed due to surface charge neutralization and adsorption of aluminum/iron-based coagulants. This formed a compact stable structure fit for a high-pressure dewatering process (Liang et al., 2019). Aluminum/iron-based coagulants can act as skeleton builders during sludge dewatering (Qi et al., 2011). For example, $FeCl_3$ can bind EPSs and form a shell of precipitate around activated sludge flocs. The precipitates created a rigid structure around the flocs, transmitting the applied stress through the filter cake under mechanical dewatering. The porous structure of the precipitate may sever as a draining media for the withdraw of water (Deneux-Mustin et al., 2001; Zhang et al., 2019b).

Furthermore, aluminum/iron-based coagulant conditioning improves the sludge dewaterability by decreasing the contents of EPSs (Liang et al., 2019; Shrestha et al., 2019). For example, conditioning by iron coagulants (e.g., $FeCl_3$ and $Fe_2(SO_4)_3$) removed LB-EPSs (Liang et al., 2019). Sludge dewaterability was also found to be related to the compositions (e.g., tyrosine/tryptophan amino acid, tyrosine/tryptophan protein, and polysaccharide) and functional groups (e.g., random coil, β-sheet, and N_{pr}) in the LB-EPSs (Liang et al., 2019). $FeCl_3$ dosed in sewage reduced the soluble EPSs (mainly soluble protein contents) of activated sludge (Niu et al., 2013; Shrestha et al., 2019). These likely contributed to the improvement of dewaterability by decreasing interstitial bond water content and sludge viscosity in sludge flocs (Shrestha et al., 2019). The EPSs were destroyed and dissolved into the liquid by the acidification effects of the iron-based coagulants (Liang et al., 2019; Wei et al., 2019), thereby reducing its water retaining capacity.

2.7 Aluminum/iron-based coagulants impact the odor generation from dewatered biosolids

Biosolids odor emission has become a concern for wastewater treatment as it causes psychosomatic effects and community opposition (Hayes et al., 2014). This review is primarily focused on the biosolids odor but not the biogas odor generated within the anaerobic digesters because these biogas odorous compounds are usually contained and destroyed in the biogas flare or combustion systems and then become less of a concern. In contrast, the biosolids management process is open to the atmosphere and thus can release odorous compounds in the course of biosolids production, storage, transportation, and land application. The odor emitted from dewatered biosolids are predominantly composed of volatile sulfur compounds (VSCs) and non-sulfur containing odorous compounds such as ammonia and amines (Gostelow et al., 2001; Stuetz and Frechen, 2001). The VSCs generated from the biosolids can generally be divided into two groups including H_2S and volatile organic sulfur compounds (VOSCs) such as methanethiol (MT) and dimethyl sulfide (Novak et al., 2006). Aluminum/iron-based coagulants have been reported to decrease VOSCs from dewatered biosolids and anaerobic digesters (Table 2.4).

Table 2.4. The impact of iron/aluminum-coagulants on VSOCs reduction from dewatered biosolids.

Coagulant	Coagulant dose*	VSOCs reduction	References
$Al_2(SO_4)_3$	4%	55%	(Chen et al., 2007b)
$Al_2(SO_4)_3$	2%	37%	(Gruchlik et al., 2013)
$Al_2(SO_4)_3$	4%	40%	(Gruchlik et al., 2013)
$Al_2(SO_4)_3$	2%	20%	(Higgins, 2010)
$Al_2(SO_4)_3$	4%	55%	(Higgins, 2010)
$Al_2(SO_4)_3$	4%	60%	(Chen et al., 2007a)
$FeCl_3$	2%	23%	(Gruchlik et al., 2013)
$FeCl_3$	4%	50%	(Gruchlik et al., 2013)

* as Al^{3+} or Fe^{3+} g g^{-1} dry solids

2.7.1 Effect of aluminum/iron-based coagulants on the odor reduction

The aluminum/iron-based coagulants can reduce the odor emission in anaerobic digesters. Previous study demonstrated that addition of 0.05 % $FeCl_3$ (g Fe^{3+} g^{-1} dry solids) and PAC (g Al^{3+} g^{-1} dry solids) reduced the VSCs production by 93% and 45%, respectively (Akgul et al., 2017). Similar observation was also reported by Abbott and Eskicioglu (2015) that 0.25 % (g Fe^{3+} g^{-1} dry solids) dose of $FeCl_3$ reduced total VSCs by ~77% under different solids retention times, and the VSCs reduction increased to ~86 % when increasing $FeCl_3$ dose to 0.32 % (g Fe^{3+} g^{-1} dry solids). It should be noticed that when sulfate-containing aluminum slats were added into the feed of anaerobic digesters, the VSCs level may be elevated as a result of the conversion of sulfate contained in aluminum-based coagulants to H_2S by sulfate reduction bacteria (Abbott and Eskicioglu, 2015; Akgul et al., 2017). Previous studies have shown that both aluminum and iron cations can reduce odor emission from dewatered biosolids (Table 2.4), i.e., up to 100% VOSCs reduction with the aluminum cations dose at 4 % (g Al^{3+} g^{-1} dry) has been achieved in a laboratory trial (Chen et al., 2007b), and 20% - 55% total VOSCs reduction with the aluminum cations dosage at 2% - 4% has been achieved in field trials (Chen et al., 2007b; Gruchlik et al., 2013; Higgins, 2010). Similarly, iron addition at the doses of 2 % and 4% (g Fe^{3+} g^{-1} dry solids) resulted in 23% and 50 % VOSC reduction in dewatered biosolids , respectively (Gruchlik et al., 2013).

2.7.2 Mechanism behind the effects of aluminum/iron-based coagulants on the odor reduction

VSCs are mainly generated from anaerobically fermented orgainc materials (Higgins et al., 2006). More specifically, proteins are the main precursors of these odorous compounds. For example, H_2S and MT are the microbial degradation by-products of sulfur containing amino acid such as methionine and cyctein (Higgins et al., 2006). Aluminum/iron-based coagulants can bind the bioavailable proteins in dewatered biosolids, which in turn reduces the pool of odor precursors (Abbott and Eskicioglu, 2015; Chen et al., 2007b; Novak and Park, 2010b; Park and Novak, 2013). Additionally, iron can react with sulfide ions to form highly insoluble FeS precipitates. This process eliminates the free sulfur and thus reduce the VSC production (Akgul et al., 2017; Higgins et al., 2006).

2.8 Concluding remarks and perspectives

2.8.1 Mechanisms of aluminum/iron-based coagulant effects on the municipal sludge anaerobic digestibility, dewaterability, and odor emission

This literature review revealed that (1) aluminum/iron-based coagulants can reduce activated sludge anaerobic digestibility likely due to the binding between these coagulants and protein fraction in the EPSs; (2) Iron-based coagulants can play both positive and negative effects on the sludge digestibility; and (3) Aluminum/iron-based coagulants can enhance sludge dewaterability and reduce the available odor precursors for odor reduction. The conclusions obtained by reviewing these literatures may aid practitioners in selecting coagulants in practice according to the sludge properties and better understanding the mechanisms behind the phenomena.

Particular attention should be paid to the negative impacts or environmental risks induced by excessive addition of coagulants. As previously mentioned, overdosing would increase the metal concentration in the effluent and in turn harm aquatic organisms (Rostern, 2017) and meanwhile lead to a 37% – 97% increase of sludge volume (Yeoman et al., 1988) besides the impacts on

sludge biodegradability, dewaterability, and odor emission. In addition, it is noteworthy that the sulfate introduced along with coagulants such as alum may increase the risk of H_2S formation and thus cause the VFA accumulation, resulting in process instability and failure. Therefore, more research on the optimization of the doses of aluminum/iron-based coagulants is necessary to strike a balance between their positive and negative effects. Moreover, aluminum-based coagulant is usually less expensive than iron-based coagulants on an equivalent dose basis (Gebbie, 2006). Therefore, a comprehensive economic analysis is needed to factor in the cost in the overall decision-making of coagulant selection specific to a given WRRF.

2.8.2 Explore the cross-effects of thermal hydrolysis pretreatment (THP) and the aluminum/iron-based coagulants on anaerobic digestion of municipal sludge

Thermal hydrolysis pretreatment (THP), which is conducted by applying high temperature (120 – 180 ℃) and pressure (1 – 9 bars) to the sludge prior to anaerobic digestion, is widely applied in the full-scale WRRFs for intensifying the treatment capacities of anaerobic digesters (Barber, 2016). As a matter of fact, THP has been applied widely in industry for more than 20 years, with a significant rise in the number of full-scale application in the WRRFs (Ngo et al., 2021). Five companies have successfully commercialized THP for sludge pretreatment including Cambi, Veolia Water, Haarsley, Sustec, and Eliquo Water. Cambi leads in THP installation with more than 40 plants in 21 countries and more than 30% of UK's sewage sludge is treated by the THP unit from Cambi (Barber et al., 2017).

As we discussed above, the slow hydrolysis rate of anaerobic digestion as a result of the binding mechanism between aluminum/iron-based coagulants and EPSs is one of the primary reasons for the poor anaerobic digestibility of the municipal sludge. Therefore, the application of THP might overcome the negative effects of aluminum/iron-based coagulants through the enhancement of sludge hydrolysis. It is known that THP offers much better hydrolysis of organic matter such as protein (Bougrier et al., 2008; Hii et al., 2014; Jeong et al., 2016; Sapkaite et al., 2017), and thus increase ammonia and alkalinity (Penaud et al., 1999). For coagulants-laden sludge, THP may release Fe^{3+} through the decomposition of Fe^{3+}-organic complex (e.g., Fe^{3+}-protein) during thermal hydrolysis, leading to Fe^{3+} precipitation with phosphate (Wang et al., 2020b). This may result in

different contaminant removal characteristics and alter the inhibitory effects of aluminum/iron-based coagulants on subsequent anaerobic digestion and sludge handling.

Sewage sludge is a complex waste with varying compositions. For example, it may contain 10% - 30% of lignin which can be decomposed to cellulose and hemicellulose (He et al., 2014). THP involves depolymerization of the sludge molecules followed by decomposition of the resultant monomers via cleavage, dehydration, decarboxylization, and deamination (Hii et al., 2014). Therefore, THP can potentially enhance the hydrolysis rate and the biodegradability of lignocellulosic biomass by cleavage of the hydrogen and ether bonds linking cellulose-lignin and cellulose-hemicellulose (Zhang et al., 2015). $FeCl_3$ addition under thermal conditions (120 – 160 ^oC) has been reported to boost the biodegradability of lignocellulosic biomass with improvement of the enzymatic hydrolysis yields (Amarasekara and Deng, 2019; Jiang et al., 2015; Shang et al., 2017). This is very likely to occur in municipal sludge THP because (i) Fe^{3+} can chelate with the phenolic groups of lignin and the hydroxyl groups in the xylan under thermal conditions, resulting in the breaking of the ether bonds between lignin and carbohydrate and thereby partially releasing hemicellulose and cellulose (Amarasekara and Deng, 2019; Tarasov et al., 2018); (ii) $FeCl_3$ provides acidic environment (Shang et al., 2017); and (iii) Fe^{3+} could be absorbed by the pyran ring of carbohydrate to form complex (Shang et al., 2017), leading to the ring-opening between the carbon-carbon bound. THP therefore could be a promising technology for improving the anaerobic digestibility of aluminum/iron-laden sludge and producing renewable products, which warrant further study.

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Chapter 3 Thermal hydrolysis for enhanced anaerobic digestion

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3.1 Introduction

Since anaerobic digestion of sewage sludge is a slow bioprocess, large bioreactor sizes have to be employed to allow long enough solids retention times (SRTs) for complete anaerobic conversion. This technical bottleneck can be unblocked by the application of thermal hydrolysis (TH) to solubilize particulate organics for faster anaerobic fermentation. The SRTs of anaerobic digester (AD) fed with TH pretreated sewage sludge can be shortened from 25-30 days to 10-15 days (Barber, 2016). TH involves heating sewage sludge at temperature between 160 and 180 ˚C for a time period of between 20 and 40 min under a pressure of 6–9 bar (Bougrier et al., 2008). TH is an well-established technology that has been applied at commercial scale for more than 20 years (Barber, 2016). There are currently more than 80 full-scale implementations worldwide (Devos et al., 2021).

TH has numerous advantages in terms of sewage sludge pre-treatment such as (i) enhancing sludge dewaterability (3−9 %) for savings on the energy for sludge drying and incineration as well as the final biosolids transport, disposal, and valorization (Higgins et al., 2011); (ii) increasing rates of digestion and biogas production (15−60%); (iii) increasing AD organic loading rates that requires smaller digester volume; (iv) better quality biosolids in terms of odor emission; (v) reduced foaming potential (Barber, 2016), and (vi) providing disinfection for Class A biosolids generation (Abu-Orf and Goss, 2012). In sum, the application of TH in tandem with AD enables water resource recovery facilities (WRRFs) to achieve energy self-sufficiency along with significant economic savings, which stimulates a growing global interest.

To apply TH, WRRFs' primary sludge (PS) and wasted activated sludge (WAS) need to be collected and dewatered to 16-18% total solids (TS). As shown in Figure 3.1, this thickened sludge is fed into a pulper in which the sludge is homogenized and pre-heated to a temperature close to 100 ˚C, using steam recovered from the flash tank. From the pulper, the warm sludge is fed to

sealed reactors in which steam is injected to heat and maintain the TH temperature at 160 to 180 ˚C under a pressure of about 6 bars for 20 to 30 minutes. After that, the sterilized and hydrolyzed sludge is released into a flash tank operated at atmospheric pressure. This sudden pressure drop leads to substantial sludge cell destruction for releasing intracellular content for enhanced digestibility and dewaterability. The steam generated by the pressure release is then returned to the pulper to preheat the incoming sludge. Leaving the flash tank, the sludge is cooled to the temperature required for AD in heat exchangers and then fed to the anaerobic digesters (Figure 3.1).

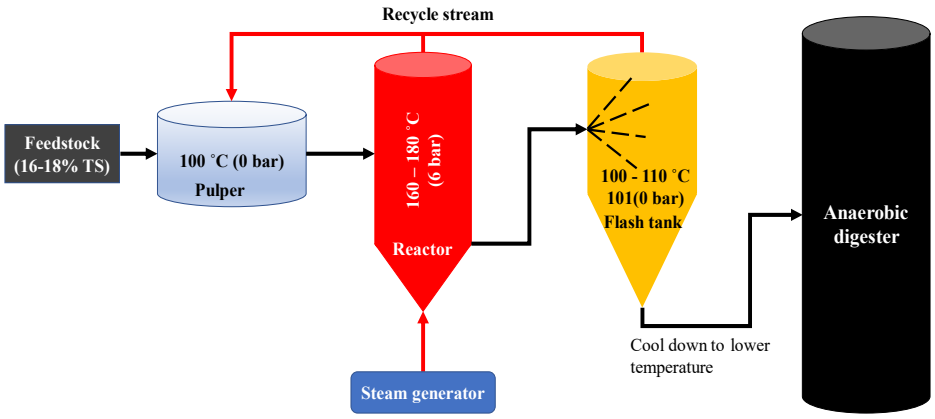

Figure 3.1. THP system design and setup

3.2 TH mechanisms

It was recognized that TH is best suited to materials which contain high concentrations of carbohydrates and proteins because it has little influence on lipids, which explains why it is more suited to WAS than PS (Barber, 2016). WAS is a microbial matrix mainly composed of extracellular polymeric substances (EPS), microorganisms, and inorganic salts. EPS is a complex containing protein, polysaccharides, lipids, nucleic acids, and humic substances, and only 30–50% of its component is readily biodegradable (Frolund et al., 1995). As the WAS temperature increases in TH, it undergoes gradual structural transformation, proceeding from solubilization of EPS, cell disintegration, broken of cell walls, and releasing intracellular proteins and nucleic acids, to

breakdown of macromolecules into amino acids, sugars, volatile fatty acids (VFAs), and other lower molecular weight organic compounds (Barber, 2016). TH temperature below 100 °C could only cause the release of EPS components in the EPS matrices rather than the lysis of bacteria cells in WAS. While, at temperature above 100 ˚C, strong hydrolysis reactions could cause the rupture of bacterial cell wall and the release of cellular organics. For the TH treatment at 160 ˚C, around 26.3~33.8% of total protein and 16.1~25.1% of total polysaccharide were reported to be hydrolyzed into smaller soluble organics in TH (Yang et al., 2019a).

In-depth analysis reveals that this enhanced solubilization phenomenon is mainly driven by three types of reactions: (i) hydrolytic reaction (Toor et al., 2011); (ii) free radical oxidation (Yousefifar et al., 2017); and (iii) sudden pressure drop associated cell rupture (Sapkaite et al., 2017). The main changes in sludge include degradation of the gel structure and release of linked water in the sludge which enhance the sludge dewaterability (Anderson et al., 2002), formation of VFAs which enhance biogas production in the downstream AD, and formation of colored compounds and refractory organic materials which conversely inhibit the biomethane production and also worsen the WRRF effluent quality if uncontrolled (Zhang et al., 2021b).

3.3 Energy Balance

To justify the applications of TH in WRRFs, its energy self-sufficient has to be considered along with other benefits TH can possibly bring. The energy consumption by the TH depends on the TS of the sludge. This is because sludge dry solids has a much lower specific heat capacity than water (Xu and Lancaster, 2009), and thus increasing the TS of the sludge can intrinsically reduce energy requirements for heating. Typically, the sludge needs to be thickened to approximately 16 ~18% TS because further thickening may incur heat transfer limitations as well as practical pumping and mixing difficulties. Even with this high TS influent, the energy benefit of integrating TH with AD is still relatively neutral as additional biogas produced through the TH enhancement will be consumed by the additional heat required for providing the high TH temperature (Barber, 2016). While the TH only provides limited benefit for energy production, it can effectively reduce the overall cost of sewage sludge management through the improvement on sludge dewaterability, digester capacity, and Class A biosolid production (Barber, 2016; Mills, 2016). It was estimated

that TH treatment can reduce around 60 ~ 70% of the water evaporation demand in sludge drying, which can significantly reduce the required drying capacity or even eliminate the drying facilities (Barber, 2016). Thus, the evaluation of TH technology should not be only limited to the biogas production. Instead, the holistic benefits for WRRFs should be taken into consideration.

3.4 TH effect on sewage sludge

The main operational parameters governing how THP improves the sludge digestibility and dewaterability include TH reaction time, pressure, and temperature. Among them, temperature is the most significant parameter.

3.4.1 TH effect on sludge particle size and solubilization

Solubility of sludge COD was found to increase in a linear-type fashion with both temperature (130 and 170 ˚C) and reaction time (10 ~ 60 min) (Lu et al., 2014). However, no further solubilization was observed beyond 170 ˚C or 60 min (Everett, 1972). Likewise, the sludge particle size also decreased as a result of TH (Barber, 2010; Neyens et al., 2004). The use of steam explosion to reduce particle size and improve sludge hydrolysis is well documented (Mason, 1926). Decreasing particle size has been linked to improved hydrolysis (Hendriks and Zeeman, 2009).

3.4.2 TH effect on sludge viscosity

The viscosity reduction has been regarded as the most important effect of the TH on sludge as it allows much higher TS to be loaded and mixed in anaerobic digesters (Stickland, 2015). It is believed that TH reduces sludge viscosity in three ways: (i) free water within the sludge fraction (Eshtiaghi et al., 2013); (ii) destroy polymers within the sludge, e.g. the denaturation of protein or destruction of EPS (Farno et al., 2015); (iii) interactions between compounds released due to heat treatment (Forster, 1983). In addition, the viscosity reduction by TH was found to be irreversible in that the yield stress of sludge exposed to heat treatment and then cooled to its initial temperature

was still lower than that of unheated sludge (Baudez et al., 2013). This phenomenon has been termed “thermal history” (Barber, 2016).

3.4.3 TH effect on sludge dewaterability

The primary energy benefit from the application of TH is the improved dewaterability which reduces downstream biosolids disposal requirements and saves drying energy by two thirds (Barber, 2016). There is unanimous agreement on the positive influence of TH on sludge dewaterability ever since the earliest work when TH was viewed as a dewatering aid but not an AD aid (Lumb, 1940; Sherwood, 1970). Sludge dewaterability improves with increasing TH temperature between 130 ˚C and 170 ˚C in a linear fashion from approximately 27 to 32% TS (Higgins et al., 2014). It was also recognized that heat treatment of sludge improves sludge dewaterability whether the sludge is digested or not (Haug et al., 1978). According to Neyens et al. (2004), TH improves sludge dewaterability by the degradation of proteins and polysaccharides from within EPS, thereby reducing its water retaining capacity (Neyens et al., 2004). EPS functions as a highly hydrated capsule surrounding the bacterial cell wall to aid the survival of the bacterial cell by preventing desiccation (Houghton et al., 2001; Wang et al., 2007). Given that EPS can be completely destroyed by autoclaving (121 ˚C) (Barjenbruch and Kopplow, 2003), it is not difficult to understand its key role in improving dewatering potential (Tian et al., 2006). However, it should be realized that anaerobic digestion is fundamentally detrimental to sludge dewaterability, i.e., although TH can greatly improve sludge dewaterability, this advantage would disappear once the sludge enters ADs. Microbial synthesis of EPS and other large molecular weight products in AD could be the reason (Zhang et al., 2021b).

3.5 TH effect on anaerobic digestion

As TH acts to enhance hydrolysis, the rate of anaerobic digestion can be accelerated such that the same amount of biogas can be produced within a much shorter time. It was reported that the digester with TH pretreatment produced almost 95% of the 20-day methane yield within just 10 days. This finding is indirectly supported by the study of Ngwenya et al. (2015) who showed

statistically insignificant difference in biogas production with TH between 10 and 18 days at the same loading rates. It should be noted that carbohydrates are degraded faster than proteins during anaerobic digestion with or without TH (Bougrier et al., 2008). As a consequence, the levels of ammonia, alkalinity, and pH increase with SRTs, posing free ammonia (FA) inhibition threat. Hence, it is suggested that anaerobic digesters following TH are optimized at SRTs of 10 ~ 12 days as it can produced approximately 95% of 20-day worth of biogas. Longer SRTs encourage protein degradation and do not result in a statistically significant increase in biogas production. However, more complete protein removal can significantly lower sludge odor potential during dewatering for both belt presses and high speed centrifuges (Chen et al., 2011). It was concluded that the sludge processed by TH and digestion had minimum odor potential based on measurements of volatile organic sulfur compounds especially when dewatered using belt presses (Chen et al., 2011). Regarding the TH potential for reactivation of marker organisms, Murthy et al. (2009) showed *E. coli* DNA density below a threshold of approximately $3\text{-}5\times10^{4}$ g^{-1} dry solids for sludge which had been processed in TH, above which reactivation was highly probable.

As the solubilization of organic materials increases when the treatment temperature is elevated, many inert compounds such as hairs, fibers, and bacterial cell walls in sewage sludge can be solubilized into the liquid phase (Van Loosdrecht and Henze, 1999). As a results, VFA release from PS was between 4 and 7 times higher than from WAS due to hydrolysis of unsaturated lipids in PS (Wilson and Novak, 2009). Meanwhile, the volatile solids reduction (VSR) of WAS also increased from 26 to 42% (van Dijk and de Man, 2010). Consequently, methane yield (m^3 methane kg^{-1} VS added) turned out to be much higher at higher TH temperature (Oosterhuis et al., 2014).

TH at 170 ˚C also successfully abated foaming issues in downstream digesters (Alfaro et al., 2014). Foam formation and stabilization requires a mixture of surface active agents, hydrophobic material, and a gas phase (Speece, 2008). Heat treatment abates foaming by destroying hydrophobic materials (Barjenbruch and Kopplow, 2003). Also, the stability of foam is dependent on viscosity which influences fluid drainage from a bubble layer. It is well-known that TH significantly reduces viscosity (Pugh, 1996).

3.6 Side effects of TH

The TH technology may induce a series of side effects including formation of high residual ammonia and refractory compounds in the centrate, which impact mainstream effluent quality and UV-disinfection (Yan et al., 2022). This can be attributed to the formation of inhibitory and recalcitrant soluble compounds and explained by Maillard reaction in TH (Zhang et al., 2020a).

3.6.1 Free ammonia inhibition

As TH allows an increase in loading rate due to viscosity reduction (Dawson and Sotiriadis, 2007) and increases the solubility of proteins (Lu et al., 2015), nitrogen from proteins and other organic materials is released as ammonium during the free radical formation stage of TH (Toutian et al., 2020). This ammonium release is particularly significant with WAS as it contains a high concentration of proteins in the bacterial cells (Liu et al., 2012b). The concentration of crude protein in WAS is around 68.68 g kg^{-1}, which is about two times higher than in kitchen waste and five times higher than in vegetable and fruit residue (Liu et al., 2012b). As TH improves the breakdown of those proteins (Bougrier et al., 2008), an increase in ammonia and also alkalinity is noted, resulting in a pH rise which shifts the equilibrium from ammonium to its free state. Having no charge, FA diffuses easily into a cell and once there ionizes to form ammonium resulting in an intracellular pH imbalance and in turn stimulates a K^+/H^+ anti-porter mechanism (Barber, 2016).
A wide range of FA concentrations has been reported as being inhibitory. Early work has suggested a FA concentration of 150 mg L^{-1} to be inhibitory to anaerobic digestion (McCarty and McKinney, 1961). Chen et al. (2014) reported that a threshold of FA which could be tolerated as high as 620 mg L^{-1}, far exceeding the typical FA range in digestion following TH. Other than pH, FA inhibition appears to be influenced by acclimation (Zhang et al., 2014a), temperature (Angelidaki et al., 1993), feedstock nutrient content (Banks et al., 2012), and seed inoculum (Yenigun and Demirel, 2013). These variables make FA comparison between studies difficult.

One way to relieve FA inhibition is to reduce SRT of AD. This is because the degradation of carbohydrates occurs in preference to the breakdown of proteinaceous materials as would be

expected from the Gibbs free energy for the relevant reactions (McCARTY, 1971). Total ammonia nitrogen levels increased from 1500 to 2500 and 3000 mg L^{-1} as AD SRT increased from 10 to 15 and 18 days. Another way is to feed carbon-rich substrate to lower pH (Chen et al., 2014). Thus can be seen, FA accumulation may not be a major problem for TH-AD process depending on the solids loading and system acclimation status. An appropriate inoculum is also important for stable AD performance during both startup period and long-term operation. According to Oosterhuis et al. (2014), no inhibition and lag phase were observed during the startup of a new AD system for digesting TH sludge when the inoculum was collected from a THP-AD system.

3.6.2 Melanoidin formation

One major drawback of using TH is the formation of colored and recalcitrant dissolved compounds (Zhang et al., 2020a). A deep analysis reveals that these refractory compounds commonly contain nitrogen and aromatic rings which are basic chemical constituents of melanoidins. Melanoidins are the final products of the Maillard reaction and defined as brown colored, nitrogenous high molecular weight compounds. It has an empirical formula of $C_{17\text{-}18}H_{26\text{-}27}O_{10}N$ and molecular weight of 5-40 kDa (Cammerer et al., 2001; Shana et al., 2013). Due to the complex structure and xenobiotic nature, melanoidins are generally refractory to biodegradation (Chandra et al., 2008). In addition, melanoidins possesses anti-oxidative capability which makes it toxic to many microorganisms involving in bioprocess (Sirianuntapiboon et al., 2004). Melanoidin production occurs in the typical reaction range of TH of 140 - 165 ˚C. Such refractory compounds can bring in three main problems for WRRFs: (i) inhibition of methane production; (ii) an increase in effluent nitrogen of the subsequent AD; and iii) failure of UV disinfection (Abelleira-Pereira et al., 2015; Dwyer et al., 2008). These recalcitrant dissolved compounds cannot be digested by anaerobic digestion, and are additionally toxic for methanogenic bacteria, leading to inefficient degradation reactions. Therefore, a high fraction of nitrogen and chemical oxygen demand (COD) will remain unchanged and threaten their permissible levels in the WRRF effluent. According to Dwyer et al. (2008), the refractory nitrogen containing organic compounds was elevated by 50% in the effluent of final settling tank, and the UV-transmission decreased by 18% during the post-treatment process, upon the commissioning of THP in a full-scale plant.

The Maillard reaction is a collection of several sub-reactions, which take place in three stages (Nursten, 2005). The kinetics of the Maillard reaction can be considered as three steps, and elevated temperature (> 70 ℃) is generally favored in each step: (i) the early-stage for Schiff base complex and Amadori compound from amino group and sugar (Ge and Lee, 1997); (ii) an intermediate stage for color formation through a range of reactions to form low molecular weight (< 3.5 kDa) melanoidins (Wedzicha and Leong, 2005), and (iii) an advanced stage to form high molecular weight (> 10 kDa) melanoidins through polymerization (Hayase et al., 2006; Tressl et al., 1998) and/or cross-linking of low molecular weight melanoidins (Hofmann, 1998a; b). The products of this stage are brown with strong UV-light adsorption capacity. During TH, one or more reaction stages can occur simultaneously that produce a mixture of final products.

Generally, sludge biodegradability increases with TH temperature starting from 100 ◦C until 175 ◦C, after which the sludge biodegradability would be deteriorated due to the elevated formation of melanoidins (Higgins et al., 2017). Thus can be seen, Maillard reaction and TH reaction proceed concurrently but in opposite ways. Therefore, TH temperature needs to be optimized to balance the improvement in sludge solubilization and melanoidins formation**.** Currently, the overwhelming consensus is that the optimal operating temperature for TH is from 165 ◦C to 180 ◦C (Neyens and Baeyens, 2003). As a result, most of the commercial TH (CambiTHP®, Exelys™, Bio Thelys™, and LysoTherm®) are set up at 165 ◦C, which theoretically should result in the production of melanoidins (Barber, 2016; Lu et al., 2015).

These recalcitrant dissolved compounds generally can be controlled in two locations in WRRFs: (i) TH reactors where they are formed and (ii) post-treatment process where they remain. Solutions can be developed based on the specific condition. Within TH reactors, the operational conditions, such as temperature and holding time (Dwyer et al., 2008), pH (Martins et al., 2000), metallic and oxidant contents (Kwak and Lim, 2004) can be modified to reduce the formation of refractory compounds. Theoretically, a lower temperature can reduce the reaction kinetics of Maillard reaction and result in less melanoidins production. Generally, at relatively low temperature (< 140 ˚C), the reaction may stop at halfway and the low molecular weight compounds are the main products (e.g., amadori produtcs) (Zhang et al., 2020a). At higher temperature, the intermediates further polymerize to form larger molecular weight compounds (i.e. melanoidins) (Coca et al.,

2005). Dwyer et al. (2008) reported that lowering TH temperature from 165 ˚C to 140 ˚C could reduce the TH effluent color by 70% without significantly reducing the anaerobic biodegradability and degradation kinetics of the sludge. pH is another important factor that influences the Maillard reaction and final products. Depending on the pKa, the aminos of a specific compound can be protonated, and it may gradually lose the reactivity with the decrease of pH. According to Martins et al. (2000), there is a positive exponential correlation between the unprotonated aminos and pH in the range of 5~8. This suggests a slight decrease in pH may effectively reduce the reactive aminos and the production of melanoidins. Metallic ions are widely used in sludge handling processes to assist sludge dewatering, phosphorus precipitation and odor mitigation (Metcalf et al., 2014). Some of the metallic ions, e.g., Mg^{2+}, Cu^{2+}, Ca^{2+}, Fe^{3+} and Al^{3+}, can effectively coagulate with the anionic melanoidins and the intermediates of Maillard reaction (Obrien and Morrissey, 1997). Therefore, the addition of metallic ions after TH treatment would also be a potential strategy to reduce melanoidins in sludge liquor. Within the AD centrate post-treatment processes, advanced oxidation processes (AOPs) (M'Arimi et al., 2020) and other physicochemical process, e.g. coagulation, absorption, can be applied to directly mitigate the inhibition of residual compounds on biological nitrogen removal process and UV-disinfection (Zhang et al., 2018b). The recalcitrant organic compounds could also be removed by reverse osmosis (RO) and nanofiltration (Zhang et al., 2020b).

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Chapter 4 Odor generation, identification, and control during biosolids production

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4.1 Introduction

The unpleasant smell released from wastewater treatment plants (WWTPs) can lead to the deterioration in quality of life and depreciation of the real estate values in the neighboring communities (Gostelow et al., 2001). The primary and secondary sludge processing and management lines in WWTPs are major contributors to odor generation and emission (Lebrero et al., 2011). The anaerobic biological reactions occurring during the sludge handling processes break down sulfurous and nitrogenous substances such as urea, protein, and amino acids, which are precursors of sulfurous and nitrogenous odorous compounds (Ren et al., 2019). Once formed, these odorous compounds could be released to the atmosphere in the course of the sludge dewatering, storage, and land application (Fisher et al., 2017).

In general, the odorous compounds generated from the anaerobic digesters and dewatered biosolids can be categorized into three groups: (1) volatile sulfur compounds (VSCs), including hydrogen sulfide (H_2S) and volatile organic sulfur compounds (VOSCs) such as methanethiol (MT, CH_4S) dimethyl sulfide (DMS, C_2H_6S), and dimethyl disulfide (DMDS, $C_2H_6S_2$) (Higgins et al. 2006); (2) nitrogenous compounds such as ammonia (NH_3) and trimethylamine (TMA, C_3H_9N) (Chang et al., 2005; Rosenfeld and Suffet, 2004); and (3) other organic compounds such as terpenes, acids, aldehydes, alcohols and ketones (Rosenfeld and Suffet, 2004). Among these odorous compounds, the sulfurous and nitrogenous compounds are usually regarded as the major odor-causing substances (Adams and Witherspoon, 2003). These two groups of odorous compounds, therefore, are the focus of this section. In particular, the characteristics and quantification methods of these

odorous compounds, the factors regulating their generation, as well as the odor reduction and control strategies are discussed.

4.2 Biosolids odor basics

4.2.1 Characteristics of odorous compounds

VSCs are recognized as key odor-causing compounds produced during the anaerobic digestion of the municipal sludge or the storage of dewatered biosolids (Higgins et al., 2006). VSCs are characterized by the disgusting smell and low odor detection concentration which is defined as the lowest concentration perceivable by human sense of smell (Table 4.1). For example, H_2S is a colorless, flammable, and hazardous gas with a “rotten egg” smell. MT, DS, and DMDS are also colorless gases with a disagreeable odor like “rotten cabbage”. The odor detection threshold concentration of VSCs were reported to vary from 0.00002 to 0.21 ppm (McGinley and McGinley, 2004). Ammonia and TMA make up most of the nitrogenous odors (Rosenfeld and Suffet, 2004). Ammonia produces a pungent medicinal odor with an odor detection threshold concentration as low as 0.038 ppm (Rosenfeld and Suffet, 2004). TMA is a colorless gas with a fishy smell. The odor detection threshold concentration of TMA varies from 0.00021 to 0.00044 ppm (Kim et al., 2003; Leonardos et al., 1974).

Table 4.1. Most common odorous compounds found in the WWTPs

Odorous compounds		Characters	Odor detection threshold (ppm)	Literatures
VSCs	H_2S	Rotten eggs	0.00045 - 0.13	(Leonardos et al., 1974); (McGinley and McGinley, 2004); (Rosenfeld and Suffet, 2004); (Kourtidis et al., 2008; McGinley and McGinley, 2004)
	MT	Rotten cabbage	0.0021 0.00002	(Leonardos et al., 1974) (Rosenfeld and Suffet, 2004)
	DMS	Rotten cabbage	0.00011 0.001	(Kim et al., 2003) (Rosenfeld and Suffet, 2004)
	DMDS	Rotten cabbage	0.0064 0.000026	(Kim et al., 2003) (Rosenfeld and Suffet, 2004)
	Carbon disulfide	Disagree, sweet	0.21 0.0077	(Leonardos et al., 1974) (Rosenfeld and Suffet, 2004)
Nitrogenous compounds	Ammonia	Pungent	46.8 0.038	(Leonardos et al., 1974) (Rosenfeld and Suffet, 2004)
	TMA	Fishy	0.00044 0.00021	(Kim et al., 2003) (Leonardos et al., 1974)

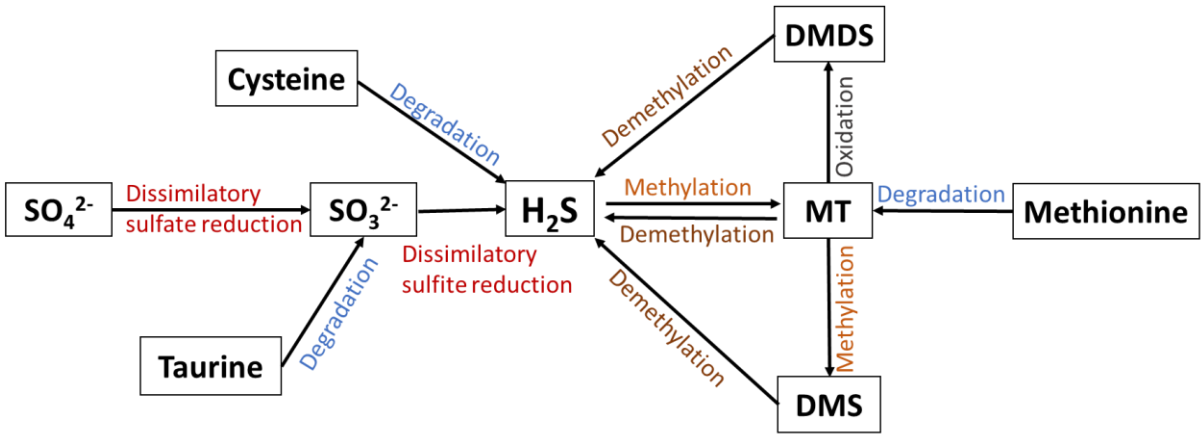

Figure 4.1. Pathways for the turnover of volatile sulfur compounds

4.3 Odor sampling and quantification

In Odor quantification is important for assessing or controlling odor emission. Many odor sampling and quantification methods have been used to determine the presence and concentration of odorous compounds. These methods usually involve headspace sampling, flux hood chamber sampling, as well as gas chromatography (GC) and sensory measurements.

4.3.1 Sampling

The gas emitted from anaerobic digesters, digested sludge, and dewatered biosolids can be collected using the static headspace method (Figure 4.2a) (Adams and Witherspoon, 2003; Glindemann et al., 2006), the summa canisters (Figure 4.2b) (Han et al. 2020), the flux hood chamber (Figure 4.2c) (Kim et al., 2003; Rosenfeld et al., 2001), as well as using the real-time probes (Hamel et al., 2004; Maulini-Duran et al., 2013; Rincón et al., 2019a). The static headspace method is often applied for ex-situ sampling in the labs, while the flux hood chamber, the summa canisters, and the probe methods are mainly applied for onsite sampling or analysis.

The static headspace analysis is a technique for sampling and examining the volatile substances associated with a solid or liquid samples over time (Figure 4.2a). The actual headspace itself is the volume of vapor or gas above the sample. The static headspace method operates by placing the samples into a sealed glass jar, and then the odorous compounds concentrations in the headspace of the sealed jar are extracted and monitored over time to obtain the odor concentration profiles along with the time (Figure 4.2a) (Luo et al., 2021). A gas bag can be connected to the glass jar for the gas pressure equalization, and a needle syringe can be used for daily headspace sampling through a rubber stopper (Figure 4.2a) (Luo et al., 2021).

A summa canister is a stainless-steel container that has the internal surfaces specially passivated using a “Summa” process (Figure 4.2b). This process combines an electropolishing step with a chemical deactivation step to produce a surface that is nearly chemically inert. A summa surface has the appearance of a mirror: bright, shiny, and smooth (Figure 4.2b). The chemical inert nature

of a whole air sample container is crucial to minimizing reactions with the sample and maximizing recovery of target compounds from the container (Wang and Austin, 2006). The sampling canisters and valves are made of stainless steel, which is sturdy and durable and can adapt to the harsh field environment. The canister is prepared for sampling by evacuating the contents to a vacuum of approximately 29.9 inches of Mercury (in Hg). Opening the stainless-steel bellows valve allows the air sample to enter the canister. Flow controllers can be utilized to restrict the flow and allow for collection at a desired flow rate or over a desired range of the odorous compounds. When the sample has been collected, the valve is closed, and the canister is returned to the laboratory for lab analysis (Figure 4.2b).

The flux hood chamber is a device commonly used to measure emission of the odorous compounds directly generated in the field. This method is recommended by the United States Environmental Protection Agency (US EPA) (Klenbusch, 1986). Gaseous emissions are collected from an isolated surface area with an enclosure device called an emission isolation flux chamber (Figure 4.2c). Clean, dry sweep air or nitrogen is added to the chamber at a fixed, controlled rate (e.g., 0.005 m^3/min). The volumetric flow rate of sweep gas through the chamber is recorded and the concentration of the constituent of interest is measured at the exit of the chamber. The emission rate is calculated based upon the surface area isolated, the sweep air flow rate, and the gaseous concentration measured. An estimated average emission rate for the area source is calculated based upon statistical sampling of a defined total area.

The real-time probe methods generally refer to the sampling and detection methods via the odor sensors such as Jerome model 631-X analyzer (Fisher et al., 2018a; Fisher et al., 2018b) and the industrial scientific iTX-T82 sensor (Maulini-Duran et al., 2013) that were used for real-time monitoring H_2S and NH_3 in the field, respectively.

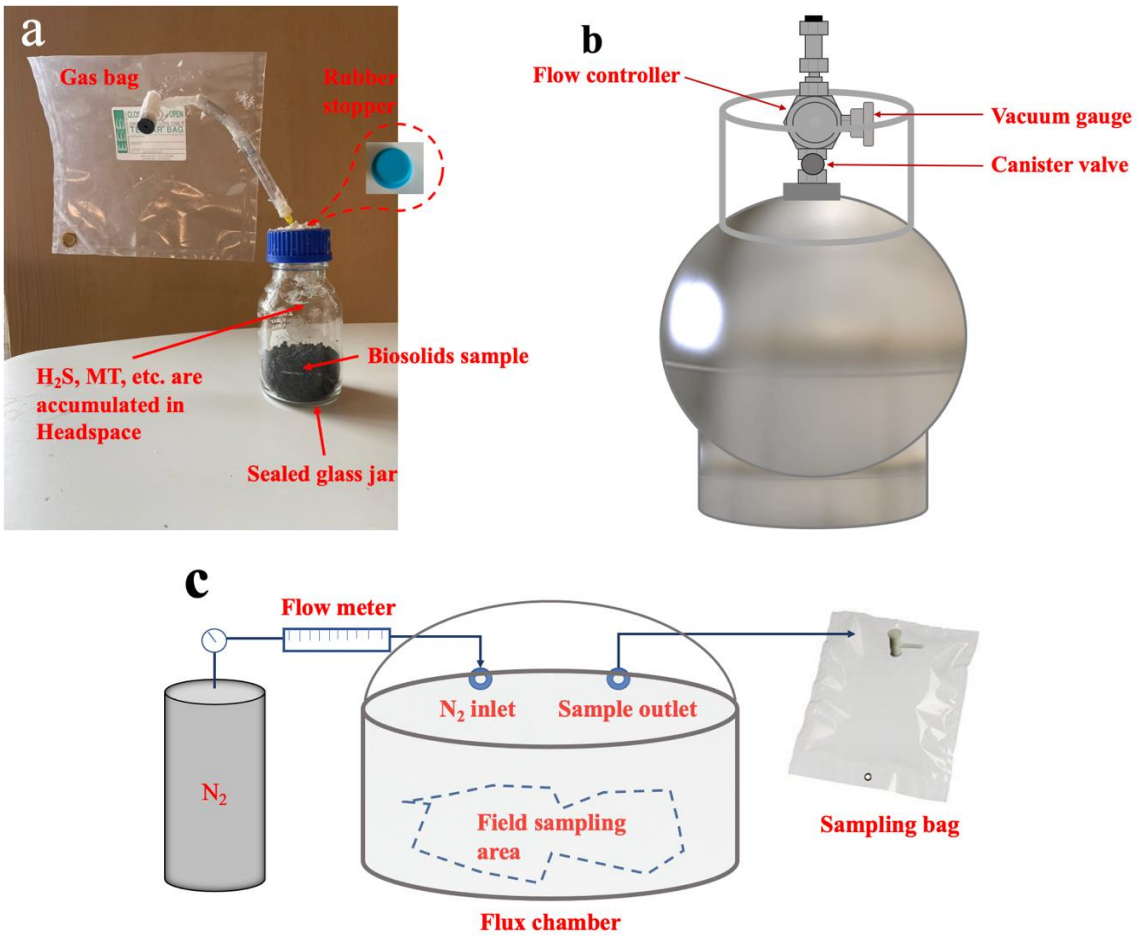

Figure 4.2. Example sampling methods including (a) static headspace sampling, (b) summa canister and, (c) flux chamber sampling

4.3.2 Measurement

Sensory measurement and instrumental analysis have been used to characterize and quantify odor. Sensory measurements rely on human response to odor while chemical analytical measurements rely on the determination of the individual odorous compound level.

Sensory measurements rely on the human odor detection ability from a selected panel as the odor detectors. The sensory measurements include subjective and objective measurements (Gostelow et al., 2001). Subjective measurements are conducted in a way that the human noses are used to indicate the odor intensity without using other equipment, while objective measurements such as

threshold olfactometry uses the human noses in conjunction with other lab device and dilution equipment (Gostelow et al., 2001). Threshold olfactometry is considered as a primary choice for odor attribute measurements (Quality, 2003; St. Croix Sensory, 2003). Odor intensity in this method is expressed in terms of the number of dilutions of odor-free air required to reduce the sample to the odor detection threshold concentration, namely the lowest concentration perceivable by the human sense of the smell. Sensory measurements are mainly used for preliminary identification and ranking of odor importance because of the poor repeatability and high subjectivity induced by different experimental designs, panel selection, and test procedure (Gostelow et al., 2001). Besides, sensory measurements cannot provide information about the chemical components of a gas mixture to determine the sources of odor emissions.

Instrumental measurements quantify the odorous compounds using either GC equipped with different detectors or GC coupled with Mass Spectrometry (MS), Proton Transfer Reaction Time of Flight Mass Spectrometer (PTR-TOF-MS), and Selected Ion Flow Tube Mass Spectrometry (SIFT-MS) for detection of different odorous compounds (Table 4.2) (Novak et al., 2012; Zhang et al., 2020c; Zhang et al., 2018a). GC coupled with detectors such as flame photometric detector (FPD), flame ionization detector (FID) (Shou and Qiu, 2020), sulfur chemiluminescence detector (SCD) (Fisher et al., 2018a), and electrochemical detector (ED) (Rincón et al., 2019b) has been widely used to determine the concentrations of various types of odorous compounds (Luo et al., 2021; Zhang et al., 2018a). However, this method does not allow real-time detection (Brilli et al., 2014). Hereto, flux hood chamber in Figure 4.2b integrated with PTR-TOF-MS (Byliński et al., 2019) or SIFT-MS (Langford et al., 2020) allows to detect a wide range of odorous compounds (DMS, DMDS, MT and NH_3) in a real-time fashion. PTR-TOF-MS uses gas phase hydronium reagent irons which are produced in an ion source for online monitoring of VOCs in ambient air (Brilli et al., 2014; Soukoulis et al., 2013). SIFT-MS involves the chemical ionization of trace volatile compound by selected positive precursor ions. This method can be used for diverse odor compounds at extremely trace levels in air with higher sensitivity than PTR-TOF-MS and GC-MS (Billiau and Mcewan, 2020). Based on the data obtained from these methods, the odor activity value (OAV), calculated as the ratio between the concentration of individual substance and the odor detection threshold, has been used to evaluate the contribution of different odorous compounds to the odor profiles. (Rincón et al., 2019b; Wang et al., 2020a). However, it is still

challenging for these techniques to investigate the unknown odor chemicals in gas mixture and chemicals with concentrations lower than the instrumental detection limit (Brattoli et al., 2013).

Table 4.2 Summary of odor sampling and detection methods.

Sampling methods	Odorous compounds	Applications	Detection methods	Literature
Static headspace sampling	DMS	Stored digested/dewatered biosolids	GC+FID	(Duran et al., 2006)
Flux hood chamber + nalophan bag	DMS, DMDS	Digested/dewatered biosolids	GC+SCD	(Fisher et al., 2018a)
Static headspace sampling + pressure tight bottles	DMS, DMDS, H_2S, MT	Digested sludge/dewatered biosolids	GC-MS	(Novak et al., 2004)
Summa canisters	NH_3, H_2S, MT, DMS, DMDS	Digested sludge after THP	GC+FPD	(Han et al., 2021)
Flux chamber headspace+adsorption tubes	DMDS, DMS, NH_3, TMA	Digested biosolids	GC-MS	(Rosenfeld et al., 2001)
Static headspace sampling		Dewatered biosolids	GC-MS	(Wilson, 2006)
Flux hood chamber + sorbent tubes	MT, DMS, DMDS	Dewatered biosolids	GC-MS	(Barczaka et al., 2021)
Flux hood Chamber	2,4,6-Trichloroanisols	Stabilized dewatered sludge	PTR-TOF-MS	(Byliński et al., 2019)
Static headspace sampling	MT, DMDS	Dewatered biosolids	GC-MS	(Bishnoi, 2012)
Summa canisters	MT, DMS, DMDS	Digested biosolids after THP	GC+FPD	(Han et al., 2020)

	MT, DMS, DMDS	Digested biosolids after THP	GC+FPD	(Li et al., 2020)
Flux hood chamber + sorbent tubes	H_2S, DMS, DMDS	Digested/dewatered biosolids	GC-MS	(Fisher et al., 2017)
Flux hood chamber	Alkanes, Aromatics, Ketones	Digested/dewatered biosolids	Jerome model 631-X analyzer	(Fisher et al., 2018a; Fisher et al., 2018b)
Real-time probe	H_2S	Dewatered sludge composting	Dynamic olfactometer	(Rincón et al., 2019a)
Real-time probe	NH_3	Composed Raw sewage sludge	Industrial Scientific sensor	(Maulini-Duran et al., 2013)
Static headspace sampling	NH_3	Biosolid storage	GC-MS	(Higgins et al., 2008)
Static headspace sampling	H_2S, DMS, DMDS	Biosolid storage	GC+FID	(Higgins et al., 2006)
Flux hood chambers+alophan odor bags	MT, DMS, DMDS	Stabilizedand stored dewatered biosolids	SIFT-MS	(Langford et al., 2020)
Flux hood chambers+alophan odor bags	NH_3, DMS, DMDS, TMA	Stabilized and stored dewatered biosolids	Olfasense olfactometer	(Billiau and Mcewan, 2020)
In situ		Dewatered biosolid land application sites	Nasal Ranger® Field Olfactometer	(Hamel et al., 2004)
Static headspace sampling +nalophan bags	H_2S, DMS, DMDS	Digested sludge composting	GC+ED	(Rincón et al., 2019b)

Static headspace sampling +nalophan bags		Digested sludge composting	Dynamic olfactometer	(Rincón et al., 2019b)
Flux hood chamber	MT, DMS, DMDS	Dewatered biosolids application	GC-MS	(Rosenfeld et al., 2001)
Static headspace sampling	H_2S	Biosolids stabilized with lime	GC-MS	(Krach et al., 2008)

4.4 Crucial factors regulating odor generation during biosolids processing

Odor precursors such as sulfate and proteins are responsible for the generation of odorous compounds in anaerobic digesters and dewatered biosolids (Burgess et al., 2001; Higgins et al., 2008). Therefore, operational parameters, such as solids retention time (SRT) and temperature used for anaerobic digestion, the types of dewatering equipment, and biosolids storage conditions (e.g., lime mixing conditions and cake storage time), may affect the odor generation by regulating the turnover of protein and sulfate.

4.4.1 Odor controlling parameters for anaerobic digesters

The elevated temperature used in anaerobic digestion has been reported to increase the production of VSCs in the biogas (Iranpour et al., 2005a; Kumar et al., 2006; Parker and Wu, 2006). For example, the concentration of H_2S detected in biogas operated under thermophilic conditions tripled that under mesophilic conditions (Parker and Wu, 2006). Iranpour et al. (2005a) reported that a rapid increase of the temperature from 54.8 ˚C to 58.8 ˚C within two weeks caused an increase of VSCs, most notably MT, in full-scale thermophilic anaerobic digesters (Iranpour et al., 2005a).

Based on the mass balance, it can be expected that an increase of VSCs in biogas should lead to a decrease of VSCs in the biosolids (Wilson, 2006). This has been repeatedly confirmed in experiments. For example, the VOSC emission from biosolids digested at 53°C was 83% and 71% less than from those digested at 35 ˚C and 49 ˚C, respectively (Wilson, 2006). Likewise, Kumar et al. (2006) reported that the sludges digested under thermophilic conditions produced approximately 30% less odorous compounds (e.g. H_2S, MT, DMS and DMDS) than that digested under mesophilic conditions.

A long SRT used in anaerobic digesters generally decreases the odor generation during both anaerobic digestion and biosolids dewatering processes (Adams et al., 2007; Adams, 2008; Ahmad et al., 2016; Higgins et al., 2005a; Verma et al., 2006; Zhang et al., 2020c). For example, the concentration of VSCs (e.g., H_2S, DMS, DMDS) decreased with the increase of SRT from 17.4 to 20.8 days in the semi-continuously-fed mesophilic digesters (Ahmad et al., 2016). In addition, increasing SRT from 15 to 30 days during mesophilic anaerobic digestion resulted in a 30% reduction of VOSCs emissions from dewatered cakes (Adams, 2008). Technically, longer SRT usually results in higher volatile solids reduction and thus the lower protein residual in the effluent of the digesters, which explains the decrease of VOSCs emission from dewatered biosolids (Verma et al., 2006).

SRT may also affect odor emission by regulating the activities and the structure of the anaerobic microorganisms in anaerobic digesters (Lee et al., 2011; Vanwonterghem et al., 2015; Zhang et al., 2018a). For example, SRT directly determines the population levels of methanogens and SRB of digester (Zhang and Noike, 1994). Longer SRT decreased the MT generation during anaerobic digestion (Zhang et al., 2018a). This could be explained by the dynamic concurrence of MT production and utilization which can be explained by the maintenance coefficient of methanogens (Zhang et al., 2018a). It was reported that the large maintenance coefficient of methanogen results in the slowdown of MT production rate in anaerobic digester running at a longer SRT (Zhang et al., 2018a).

4.4.2 Dewatering equipment

The types of dewatering equipment used also impact VSCs production. Murthy et al. (2013) compared the VSCs contents generated from three different dewatering equipment including high-solids centrifuge, low-solids centrifuge, and belt filter press (Murthy et al., 2003). Results indicated that the highest amount of VSCs was generated from cakes produced from the high-solids centrifuge. While, no detectable VSCs was observed for cakes obtained from the belt filter press simulator (Murthy et al., 2003). The greater shear force in high-solids centrifuge than that in low-solids centrifuge and belt filter press was believed to be the reason for generating the higher VSC concentration. Briefly, the high centrifuge shear force released soluble sulfur-containing amino acids that were originally entrained within the dewatered sludge cake (Chen et al., 2011; Muller et al., 2004). Besides, the centrifuge shearing of biosolids also resulted in oxygen exposure by disrupting the solid structure, leading to the inhibition of the methanogens who plays important roles in utilizing VSCs as illustrated in Figure 4.1 (Muller and Novak, 2008).

4.4.3 Biosolids storage conditions

Lime stabilization has been used to sterilize dewatered solids for pathogen reduction prior to the land application (Erdal et al., 2004). Proper lime mixing parameters such as lime dose and mixing efficiency were found to be the main factors regulating the reduction of offensive odors in lime stabilized biosolids (Krach et al., 2008; Mangus et al., 2006; Romero-Flores et al., 2017). This is because sufficient lime dose and mixing are required to provide a homogenous distribution of a high enough pH value, e.g., 12, across the biosolids bed so as to immediately halt all microbial activities producing odor (Krach et al., 2008; Williford et al., 2007). The failure of the inhibiting odor-producing microorganism owing to the poor mixing or insufficient lime doses has been previously reported (Krach et al., 2008). However, it is noteworthy that, when amine-containing polymers were used for dewatering, the high pH-driven dissociation and volatilizing of TMA produced from the breakdown of amine-containing polymers may increase the odor production after lime stabilization as summarized in Table 4.1 (Chang et al., 2005). This is the opposite to the desire for biosolids odor control (Chang et al., 2005; Kim et al., 2003; Laor et al., 2011; Novak et

al., 2002). Choosing the polymers without an amine component should be considered to avoid this contradictory problem.

The biosolids storage time also regulates the concentrations of odorous compounds produced from biosolids cake (Adams, 2008; Murthy et al., 2003). VOSCs generated during biosolids dewatering actually can dissipate after the cake storage for 15 – 20 days, likely because of the regrowth of odor-consuming methanogenic bacteria (Erdal et al., 2008). It was observed that the VSCs production during the cake storage peaked in 3 to 8 days and then declined (Novak et al., 2006). As a consequence, storing dewatered biosolids cakes for 20 to 30 days at 22 to 25 ˚C reduced ~80% of MT, DMS, and DMDS (Novak et al., 2006). Therefore, it is recommended to extend the storage time before transportation and land application of biosolids to pass this initial VSCs peak (Fisher et al., 2019).

4.5 Strategies for biosolids odor control

Compared to the enclosed system of anaerobic digesters, the odorous compounds generated from biosolids are more likely to emit to the atmosphere during biosolids dewatering, storage, transportation, and land application. Good management practices are needed to reduce biosolids odor emissions. The following sections describe several potential odor reduction strategies that can be adopted by biosolids management practitioners.

4.5.1 Optimization of anaerobic digesters

As mentioned throughout this section, amino acids produced from the hydrolysis of proteins are the major precursors of odorous compounds in biosolids (Higgins et al., 2005a; Higgins et al., 2006). Therefore, reducing the amounts of bioavailable protein in the sludge cake offers the opportunity to reduce biosolids odor emission. More complete degradation of protein during anaerobic digestion thus allows more reduction of the odor emission from biosolids. This can be achieved by operating anaerobic digesters at relative longer SRTs (Adams et al., 2007; Ahmad et al., 2016; Verma et al., 2006; Zhang et al., 2018a), higher temperature (Iranpour et al., 2005a;

Iranpour et al., 2005b; Kumar et al., 2006; Parker and Wu, 2006), and in conjunction with THP (Bougrier et al., 2008; Wilson, 2006) or bioaugmentation (Duran et al., 2006; Tepe et al., 2008). THP applies high temperature (120 – 180 ˚C) and high pressure (6 – 11 bars) to promote protein hydrolysis. This process allows an increase of bioavailable protein for the anaerobic digestion and thus the decrease of bioavailable protein in the biosolids (Bougrier et al., 2008). Hence, high odor production in the digesters but low odor emission from the digested sludge are expected. For example, high levels of H_2S, NH_3 and MT were found in the mesophilic anaerobic digesters operated with THP (Han et al., 2021). While, the VOSCs contents in dewatered biosolids were reduced by ~90% with THP as compared to the case without THP as most of protein were removed during THP-enhanced anaerobic digestion (Wilson et al., 2006).

4.5.2 Dewatering methods

Several methods such as low-solids centrifuge (Chen et al., 2011; Forbes et al., 2007; Muller and Novak, 2008; Muller et al., 2004; Murthy et al., 2003), polymer addition (Abu-Orf et al., 2005; Chang et al., 2005), chemical conditioning (Abbott and Eskicioglu, 2015; Chen et al., 2007b; Gruchlik et al., 2013; Wei et al., 2018b), and aeration of the sludge before dewatering (Luo et al., 2021; Winter et al., 2004) can be applied to reduce the odor emission during the sludge dewatering. For example, the low-solids centrifuge operated at 1200 rpm produced about half of the VOSC emissions from the biosolids cake than the high-solids centrifuge operated at 2200 rpm. This can be attributed to the lower protein exposure under lower shear force because undigested protein was originally wrapped inside the sludge particles after the conditioning and before the centrifuge (Forbes et al., 2007).

Polymer addition can influence odor production from dewatered biosolids because polymers sequester soluble protein during dewatering and deposit this protein in the biosolids cake. As a consequence, a greater polymer dose tends to result in higher concentrations of VOSCs produced from the biosolids cake (Higgins et al., 2005b). Partial degradation of certain type of cationic polymer such as acrylamide-based polymer can also generate amine odor such as TMA (Abu-Orf et al., 2005; Chang et al., 2005). Therefore, reducing the polymer doses and avoiding the amine-containing polymers provide options to reduce the odor emission during biosolids dewatering.

Aerating the sludge prior to the dewatering process was also found to be effective in reducing peak emission concentrations of H_2S, MT, and DMS by 30% – 50% from the dewatered cake for the oxygen inhibition of the odor-producing bacteria such as SRB, which in turn help reduce the odor generation from the dewatered biosolids, as well (Luo et al., 2021; Sass et al., 2002; Zhang et al., 2014c).

Al^{3+}- and Fe^{3+}-laden coagulants are often used to chemically condition municipal sludge prior to high-pressure dewatering since the coagulation products can function as the skeleton builders to support sludge structure and reduce sludge compressibility (Wei et al., 2018a). Fe^{3+} and Al^{3+} can reduce the pool of odor precursors through binding the bioavailable proteins and also the precipitation of sulfide ions (Abbott and Eskicioglu, 2015; Chen et al., 2007b). For example, ~40 % and 23% reduction of total VOSCs concentration was observed for the biosolids dewatered with aluminum doses at the 2% – 4% g Al^{3+} g^{-1} dry solids and iron doses at the 2 % g Fe^{3+} g^{-1} dry solids, respectively (Gruchlik et al., 2013).

4.5.3 Post-dewatering odor control

After sludge dewatering, several strategies still can be employed to control odor emission include the high lime dose and sufficient lime mixing (Krach et al., 2008; Mangus et al., 2006), as well as the sufficient biosolids storage time before land application (Adams et al., 2007; Murthy et al., 2003; Zhang et al., 2020c). Other methods such as odor adsorption with activated carbon (Das et al., 2003) or wood ash (Rosenfeld and Henry, 2000) during the biosolids stabilization should also be considered. For example, 89% reduction of DMDS emission was observed during the stabilization of a mixture of biosolids and wood shaving amended with activated carbon (Das et al., 2003).

4.6 Concluding remarks

Factors contributing to odor emission and control during municipal sludge stabilization include the operational parameters of anaerobic digesters such as the temperature and SRTs used, the

dewatering equipment employed, as well as the biosolids storage conditions and stabilization methods. Several odor control strategies were proposed aiming to reduce the available protein, the primary precursor of sludge odorous compounds. In short, a long SRT and a higher temperature used during anaerobic digestion, less shear force used during biosolids dewatering, and sufficient lime doses and mixing effectiveness, optimum polymer doses and types, Al^{3+}- and Fe^{3+}-laden coagulants, and an extension of cake storage time should be considered as options for municipal sludge odor control strategies

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Chapter 5 An experimental examination of carbon diversion to primary sludge: Pros and Cons

(This chapter manuscript has been prepared)

5.1 Abstract

Redirecting wastewater organic carbon to anaerobic digesters through primary sludge (PS) production in lieu of aeration tanks has been pursued as a viable means for achieving energy neutrality in water resource recovery facilities (WRRFs). A comprehensive evaluation of the approach was investigated in this study by taking into account the solids reduction, energy recovery and savings, sludge dewaterability, and recalcitrant dissolved organic nitrogen (rDON) formation when thermal hydrolysis pretreatment (THP) was used. Experimental results revealed that increasing the PS-to-wasted activated sludge (WAS) ratios from 0:1 to 1:1 and 3:1 through chemically enhanced primary treatment (CEPT) led to residual solids increase for 9% and 16%, aeration energy savings for 35% and 60%, and energy recovery increase for 67% and 120%, respectively. Very importantly, it was for the first time reported from this study that blending PS and WAS led to excessive rDON formation during THP. Fortunately, high Al3+ doses used during CEPT precipitated most of the rDON along with orthophosphate removal which also led to sludge dewaterability improvement. Thereby, a major drawback of carbon diversion is the extra biosolids production in comparison with the scenario without diversion. Since the primary responsibility of WRRFs is discharge water quality control and solids reduction, it was concluded that a technoeconomic analysis is needed to calculate the overall gains of carbon diversion.

5.2 Keywords

Dewaterability; Digestibility; Maillard; rDON; Carbon diversion

5.3 Introduction

Public wastewater treatment annually consumed 3-4 % energy production and contributed 1 % greenhouse gas emission in the U.S. (EPA, 2022; EPA, 2013). Meanwhile, the chemical energy contained in wastewater was estimated to be 9.3 times the energy it takes to treat it (Shizas and Bagley, 2004). Therefore, harvesting wastewater energy has been proposed as a viable means for achieving energy neutral wastewater treatment. Redirecting wastewater organic carbon as much as possible to anaerobic digester (AD) through primary sludge (PS) production in lieu of aeration tanks has been pursued as a pioneer approach for energy recovery (Guven et al., 2019; Nizami et al., 2017). This is opposite to the design of many water resource recovery facilities (WRRFs) built during the first half of the 1900s when the primary focus was on water quality rather than energy management (Schmidt Jr and Dhulashia, 2020). As a consequence, many of these WRRFs are not even equipped with primary clarifiers and/or AD. Minimizing total biosolids production through carbon conversion to CO_2 in aeration tank has been a common design, making aeration a major contributor to energy consumption and greenhouse gas emission in WRRFs (Guven et al., 2019). That being said, redirecting influent organic carbon to PS not only holds promise to increase energy recovery in anaerobic digesters but also decreases electrical energy requirement for aeration, and in turn expanded WRRF capacity by reducing the organic loading upstream of the secondary process (Shewa et al., 2020).

Various primary treatment technologies have been implemented for PS production, including chemically or biologically enhanced sedimentation or mechanical screening and filtration, among which chemically enhanced primary treatment (CEPT) is the most popular as it achieves the greatest total suspended solids capture efficiency (60-90%) (Schmidt Jr and Dhulashia, 2020), is easy and economical to implement, and removes phosphorus, dissolved heavy metal, as well as many other micropollutants (Shewa and Dagnew, 2020).

While, every coin has two sides, and PS production is not an exception. Although well-established jar test methods have been developed to select the coagulant and dosage for a desired amount of PS production (Guven et al., 2019), popular coagulants such as alum ($Al_2(SO_4)_3$) are known to

reduce the sludge biodegradability through their binding of organics, especially at high dose used for high PS production (Guven et al., 2019). Although PS possesses much better biodegradability than wasted activated sludge (WAS), alum dosed into PS may further play down the overall biodegradability of the blended sludge (Luo et al., 2022). Moreover, diverting influent organics into PS is bound to increase the solid loading of AD. In recent years, full-scale thermal hydrolysis pretreatment (THP) has been broadly applied to improve the sludge digestibility and augment the capacity of AD by increasing anaerobic digestion rates (Barber, 2016). The chemical bonds between coagulants and organics are also expected to be broken by THP (Luo et al., 2022). While addressing these PS production-caused limitations, THP also brings side effects, one of which is the formation of recalcitrant dissolved organic nitrogen (rDON) (Zhang et al., 2020b). It has been recognized that rDON formed during THP is mainly from the Maillard reaction via the chemical reaction between the carbonyl groups of reducing sugar and the amino groups of proteins (Zhang et al., 2021a; Zhang et al., 2020b). This is because the typical THP conditions, e.g., 165 ˚C for 30 min, overlap with that of the Maillard reaction. More importantly, PS and WAS are mainly composed of carbohydrates and proteins, which are the precursors of carbonyl groups and the amino groups, respectively. Therefore, blending PS with WAS as commonly practiced in WRRFs provides an ideal recipe for Maillard reaction and in turn rDON production in THP (Hodge et al., 1972). rDON is responsible for total nitrogen (TN) increase in the discharge, biological nitrogen removal inhibition, and UV transmission blockage (Abelleira-Pereira et al., 2015; Dwyer et al., 2008).

Therefore, the objective of this research is to experimentally examine the pros and cons of carbon diversion to PS in terms of overall energy recovery, solids reduction, as well as dissolved compound removal. In general, three scenarios were compared in parallel, i.e., (i) WAS only without PS production; (ii) PS production to 1:1 dry mass ratio with WAS; and (iii) PS production to 3:1 dry mass ratio with WAS. Additional control experiments were also added to assist the understanding of mechanisms behind. THP was adopted in all three scenarios to reflect the state-of-the-art of the sewage sludge anaerobic digestion enhancement. The coagulant dose-dependent mass balance between PS and WAS production was also taken into consideration. Thereby, the pros and cons of each scenario were analyzed. It is the intention of this study to inform wastewater industry of not only the benefits but also the hidden pitfalls of carbon diversion with

first-hand experimental data. The findings from this study would be interesting to researchers and engineers who are considering the adoption of carbon diversion technologies in WRRFs.

5.4 Materials and Methods

5.4.1 Sludge sampling and blending

The raw PS collected from a local WRRF was dewatered using a pilot dewatering unit ES-051 (PWTECH, Rosedale, MD). The coagulant dosing was performed during this pilot PS dewatering. After a 90-day anaerobic digester startup, alum was dosed as a coagulant into the PS. Referring to results in Figure 5.1 a, b, c, and d, as soon as alum was dosed, digester performance quickly crashed with dramatic pH drop, volatile fatty acid (VFA) and soluble chemical oxygen demand (sCOD) accumulation, and biogas production cease. A closer look into the biogas composition revealed that its H_2S content has reached 35,000 ppm (Figure 5.1e), indicating it was the sulfate ions in alum that has been reduced to H_2S in anaerobic digesters and in turn crashed the digester performance. It should be realized that the sulfate ions are usually dissolved in and discharged with mainstream water and do not end up in the side stream system as observed in Figure 5.1. To rectify this artifact, from the day 200 and on, aluminum chloride ($AlCl_3$) was dosed as a coagulant to avoid H_2S formation and inhibition (Figure 5.1).

The dewatered WAS with total solids (TS) around 20% was collected from another local WRRF. The PS and WAS cakes came with 1.28 % and 1.7 % background Al^{3+} contents. Thereby, a group of WAS only sample with 1.7 % background Al^{3+} content was used to represent Scenario 1 when no PS was produced in WRRFs (Table 5.1). In order to predict the other two scenarios, a BioWin model (Envirosim Associates Ltd, Hamilton, Canada) was run in concert with a jar test to estimate the alum-dependent PS and WAS production through mass balance. Results showed that dosing external Al^{3+} into PS to 2.2% and 3.23% including background levels are required to produce PS with dry mass ratios to WAS of 1:1 and 3:1, respectively (Table 5.1). Thereby, we name these two spikes as ‘low’ and ‘high’ Al^{3+} doses, respectively. Collectively, they gave total Al^{3+} contents of

1.95% and 2.85 % in sludges blended with PS-to-WAS dry mass ratios of 1:1 and 3:1, respectively (Table 5.1). These two groups represent the low and high PS production scenarios for the two extents of carbon diversion, namely Scenarios 2 and 3 in Table 5.1. Besides the three scenarios, a group of blank without Al^{3+} dosing and a group of control with high Al^{3+} dosing were added in Table 5.1 to assist in understanding the effect of Al^{3+} dosing when PS-to-WAS dry mass ratios were fixed at 1:1. Meanwhile, two high Al^{3+} dose groups with PS-to-WAS dry mass ratios blended at 1:1 and 3:1 also can be parallelly compared to help understand the effect of the blending ratios (Table 5.1). In the end, a PS only group was also added as a control in Table 5.1 to help check the effect of blending in concert with the WAS only group.

Table 5.1. Summary of PS-to-WAS blending ratios and Al^{3+} doses used in each experimental group

Role	Group	Dry mass ratio		Individual Al^{3+} content (%)		Total Al^{3+} content (%)
		PS	WAS	PS	WAS	
Scenario 1	**WAS only**	0	1	N/A	1.7	1.7
Scenario 2	**PS:WAS = 1:1 with low Al^{3+} dose**	1	1	2.2	1.7	1.95
Scenario 3	**PS:WAS = 3:1 with high Al^{3+} dose**	3	1	3.23	1.7	2.85
Blank	**PS:WAS = 1:1 with no Al^{3+} dose**	1	1	1.28	1.7	1.49
Control	**PS:WAS = 1:1 with high Al^{3+} dose**	1	1	4	1.7	2.85
Control	**PS only**	1	0	1.28	N/A	1.28

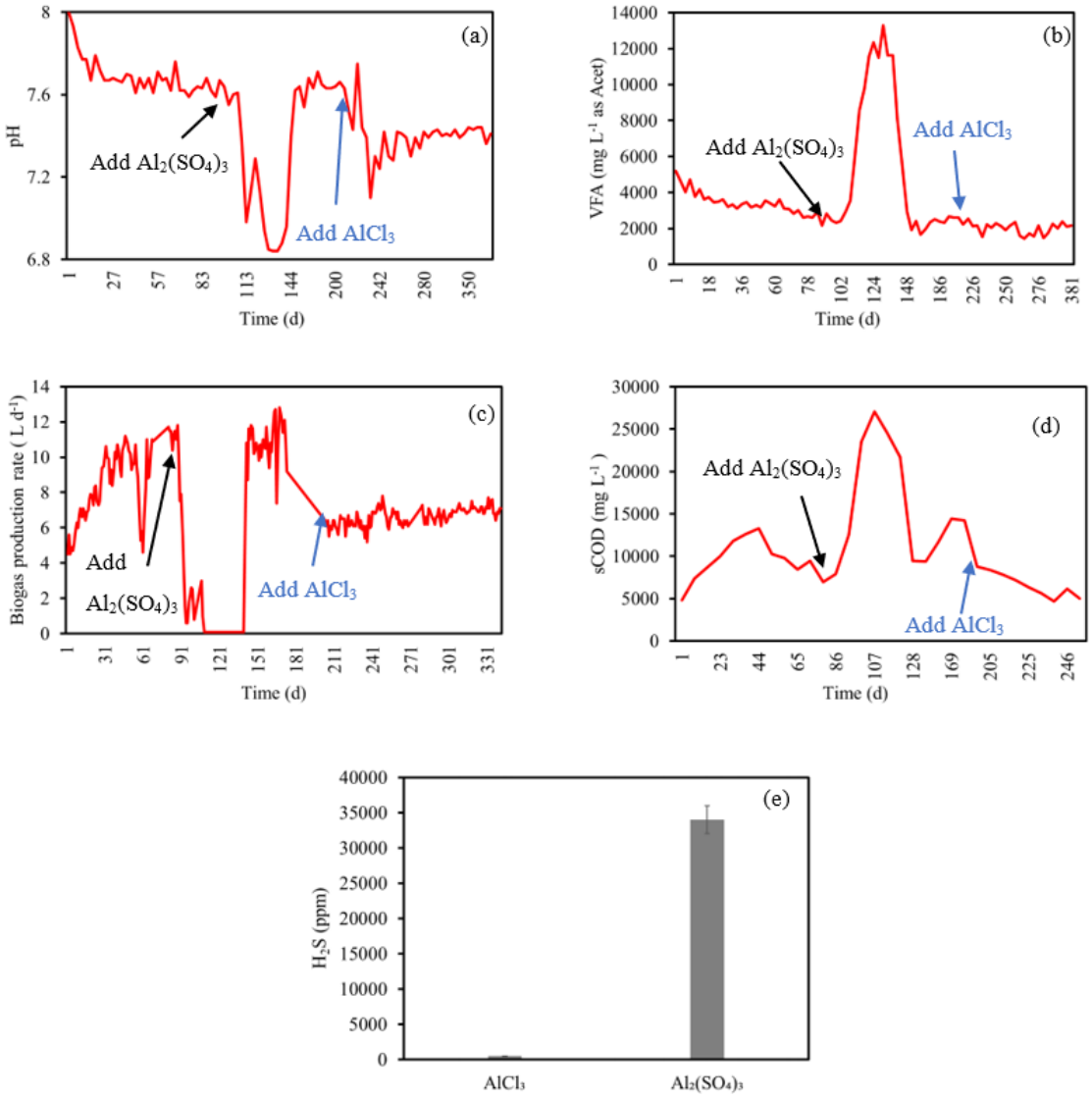

Figure 5.1. (a) pH, (b) VFA, (c) biogas production rate, and (d) sCOD profiles for the 1:1 PS-to-WAS dry mass blending ratio sludge spiked with high Al^{3+} dose using two different Al^{3+}-based coagulants; (e) H_2S concentration detected in biogas on day 100 and 290 with different Al^{3+}-based coagulant.

5.4.2 Pilot THP-AD system setup

A flow chart of the pilot scale THP-AD system operation procedures is shown in Figure 5.2. In short, dewatered PS and WAS cakes were blended and diluted with deionized (DI) water from 20% TS to 16% TS prior to being fed into a pilot scale THP facility (CAMBITM, Norway) heated with in-situ generated steam as shown in Figure 5.3 left. This THP was operated at 165 ˚C and 6 bars for 30 min. Afterwards, the treated sludge was ejected into a flash tank where it was cooled down to room temperature. The steam addition into the THP lowered the sludge TS to 12.5% in the THP effluent which was further diluted with DI water to 9% prior to being fed into mesophilic ADs. Six units of mechanically mixed ADs, each with 5 L working volume and 10 L headspace as shown in Figure 5.3 right, were operated in parallel with temperature maintained at 36.5 ± 0.3 ˚C. These ADs were inoculated with fresh effluent sludge from a full-scale THP-fed mesophilic AD. The 9% TS sludge was fed into each AD on a daily basis. The SRTs of these six digesters were controlled at 15 days.

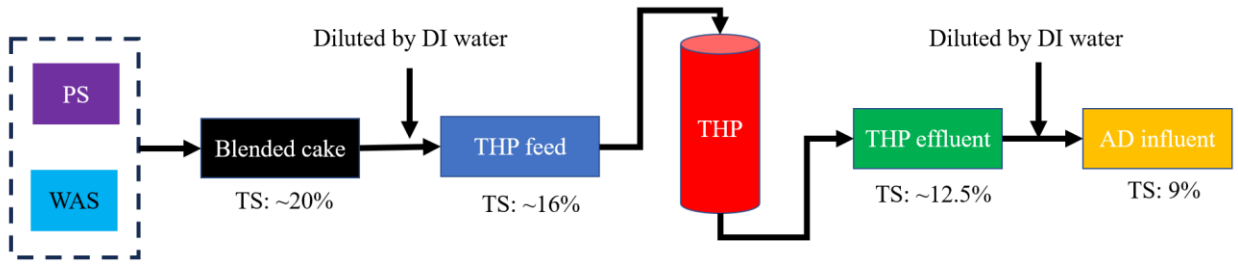

Figure 5.2. Pilot scale THP-AD system operation flow chart.

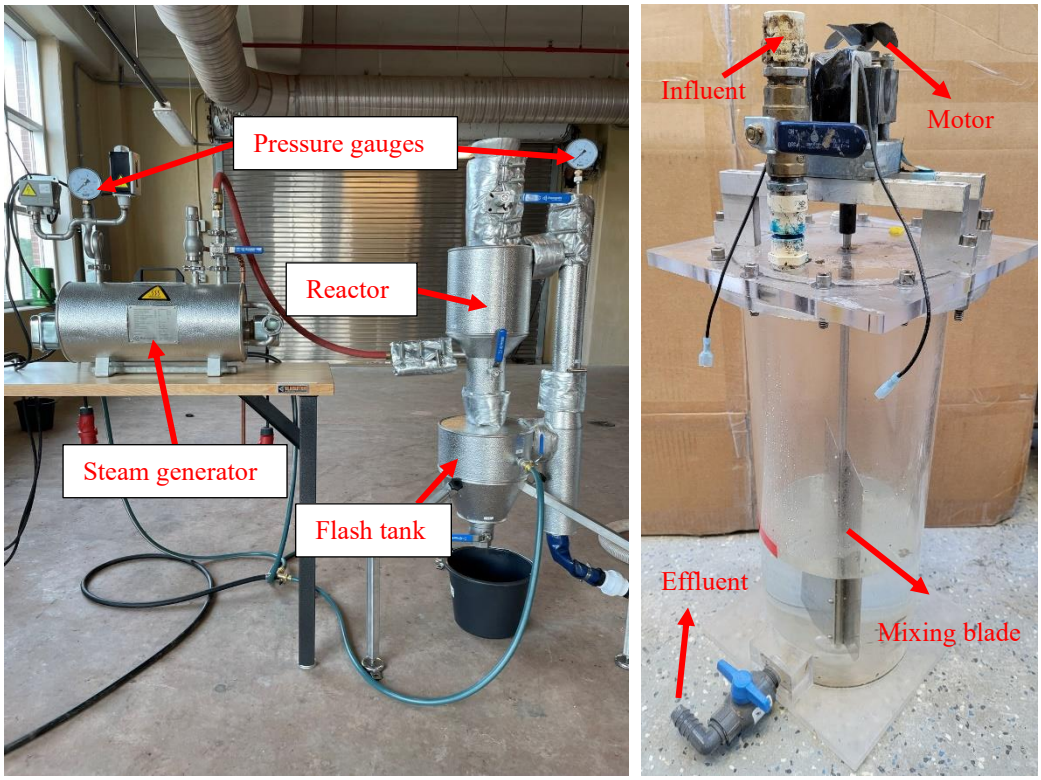

Figure 5.3. *left*: pilot scale THP setup; *right*: mechanically mixed anaerobic digester setup.

5.4.3 Chemical analysis

The concentrations of chemical oxygen demand (COD), TN, total Kjeldahl nitrogen (TKN), total ammonia nitrogen (TAN), and Ortho phosphorus (OP) were measured using the Hach test kits of TNT 822, TNT 880, TNT 832, and TNT 845 respectively (Hach, Loveland, CO). Samples for soluble substance measurement including sCOD, soluble TKN (sTKN), TAN, and OP were filtered through 0.45 μm nylon filters (Aura Industries, New York, NY). Meanwhile, pH was measured with a benchtop pH meter (AE150, Fisher scientific, Hampton, NH). TS and volatile solids (VS) were measured according to the standard methods (APHA, 2012). Besides, the biogas production rate was real-time monitored using calibrated tipping-bucket meters (Archae Press, Nashville, USA) coupled with automatic data loggers (MicroDAQ, Contoocook, NH). Moreover, CH4 content in biogas was measured using a Gas Chromatography equipped with a thermal conductivity detector (GC-2014, Shimadzu, Columbia, MD). The dewaterability of AD effluent

was evaluated by capillary suction time (CST) measured with a capillary suction timer (294-50, Ofite, TX, USA).

5.4.4 rDON quantification

As defined in our previous studies (Zhang et al., 2021a), rDON can be regarded as the dissolved organic nitrogen (DON) that can survive aerobic treatment commonly used in the secondary wastewater treatment process. Therefore, centrate was collected from the AD digestate and then exposed to fresh activated sludge for aerobic degradation until all ammonia has been full nitrified and DON level does not decrease anymore, which is regarded as the level of rDON. To obtain centrate, 300 ml of the AD effluent sample was mixed with 50 ml of polymer composed of 40% active acrylamide (4110B, Univar Solutions, Downers Grove, IL) in a commercial blender. Then, the mixture was pre-dewatered using a lab centrifuge at 5000 g for 20 min, after which the centrate was collected for rDON quantification. Because TAN concentration in the centrate was significantly greater than that of DON, the background TAN level has to be reduced to achieve an accurate DON reading because DON is calculated as the difference between sTKN and TAN. To this end, an air stripping method was used to remove TAN prior to the aerobic treatment. Briefly, pH of the centrate was adjusted to 11 with 0.1N NaOH. Then, an air flow rate of 2.7 L min^{-1} was introduced into the centrate for air stripping (Figure 5.4a). The TAN concentration was monitored daily until its level was below 200 mg L^{-1}. After that, fresh activated sludge collected from the aeration basin at a local WRRF was collected and thickened using a lab centrifuge at 2000 g for 10 min. 10g of the thickened activated sludge was inoculated as the seed into 200 ml centrate that has TAN stripped, pH adjusted to 7.5, and concentration diluted for two times to avoid inhibition based on previous experimental experience. Then, an air flow rate of 2.7 L min^{-1} was introduced into the mixed liquor through an aeration stone to provide dissolved oxygen and mixing (Figure 5.4b). During this aerobic treatment, the pH of the mixed liquor was monitored and lowered to 7.5 on a daily basis by adding 0.1N H_2SO_4. Meanwhile, the TAN, NO_3^-, and DON levels were monitored until all TAN was oxidized to NO_3^-, and DON reached a constant minimum level. A seed only group with centrate replaced by DI water was used as the control to deduct DON

contribution from the seed sludge. All experimental groups were duplicated to check data reproducibility.

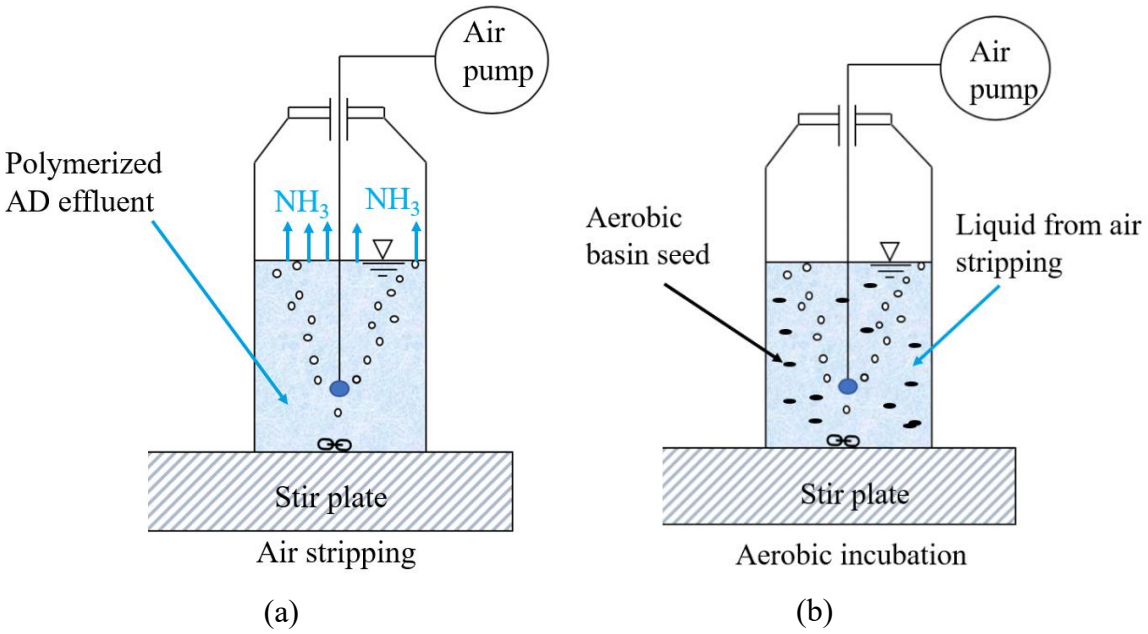

Figure 5.4. rDON test experimental design: (a) air stripping to remove TAN: (b) aerobic incubation to remove biodegradable DON.

5.4.5 Data analysis

T-test was performed to assess whether statistical difference can be found in the daily biogas production rates as a means to determine whether steady states have been reached. At steady state during day 280 and 295 in Figure 5.1c, data was collected twice a week from duplicated groups and then presented as the mean values with standard errors. The effect of steam dilution on concentration change before and after THP was taken into calculation by using sludge inorganic matters as an internal standard, i.e., the inorganic matter concentration change before and after THP can be used to calculate a dilution factor for their conservative nature.

5.5 Results

5.5.1 Effects of blending ratio and Al^{3+} dosing on THP performance

The pre- and post-THP total COD (tCOD), sCOD, TKN, TAN, and DON concentrations were measured to understand the effects of THP on sludge solubilization. As shown in Table 5.2, tCOD remained almost the same before and after THP for all groups. Similarly, TKN consisting of both protein and ammonia nitrogen remained unchanged during THP. PS exhibited higher tCOD but lower TKN than WAS because PS is known to contain a higher carbon and lower nitrogen than WAS (Pinto et al., 2016). Significant amounts of sCOD and soluble nitrogen including TAN and DON were released during THP as a result of high temperature and pressure for all groups. Consistently, more TAN and DON were released from WAS than from PS after THP as a result of hydrolysis during THP (Barber, 2016). As a results, the sludge with higher PS-to-WAS blending ratio tended to produce lower TKN, TAN, and DON concentration for the lower nitrogen content in PS. Very importantly, higher Al^{3+} doses led to lower sCOD, TAN, and DON levels in THP effluent probably due to precipitation (Table 5.2).

Table 5.2. The pre- and post-THP sludge characteristics

Groups	tCOD (mg L^{-1})		sCOD (mg L^{-1})		TKN (mg L^{-1})		TAN (mg L^{-1})		DON (mg L^{-1})	
	Pre	**Post**	**Pre**	**Post**	**Pre**	**Post**	**Pre**	**Post**	**Pre**	**Post**
PS only	157060 ± *9861*	151100 ± *6555*	147 ± *22*	18285 ± 399	4324 ± *179*	4478 ± *221*	7 ± *1*	308 ± *14*	35 ± *2*	1006 ± *21*
WAS only	140481 ± *5321*	136500 ± *4214*	142 ± *4*	28774 ± 694	7529 ± *165*	7248 ± *197*	15 ± *0.2*	649 ± *17*	46 ± *7*	1863 ± *101*
PS:WAS = 1:1 with no Al^{3+}	166757 ± *8689*	154000 ± *9500*	173 ± *16*	24304 ± *260*	6535 ± *198*	6220 ± *52*	11 ± *0.5*	427 ± *21*	34 ± *6*	1550 ± *35*
PS:WAS = 1:1 with low Al^{3+}	154364 ± *6416*	149200 ± *1565*	58 ± *14*	24750 ± *525*	6445 ± *114*	6730 ± *64*	9 ± *0.3*	383 ± *6*	34 ± *6*	1610 ± *30*
PS:WAS = 1:1 with high Al^{3+}	160560 ± *5121*	151600 ± *5698*	70 ± *10*	15237 ± 588	5335 ± *105*	5074 ± *142*	14 ± *0.1*	318 ± *25*	30 ± 5	1170 ± *117*
PS:WAS = 3:1 with high Al^{3+}	154364 ± *6932*	149200 ± *5748*	52 ± *6*	12800 ± 125	5290 ± *102*	4645 ± *111*	12 ± *0.2*	396 ± *44*	32 ± *4*	1092 ± *35*

5.5.2 Effects of blending ratio and Al^{3+} dosing on volatile solids reduction and CH_4 yield

Volatile solids reduction (VSR) and CH_4 yield are two key parameters indicating the THP-AD performance as they represent the solids reduction and energy production efficiencies, respectively. As can be seen in Figure 5.5a, PS exhibited superior VSR and CH_4 yield to WAS, which is expected. For the sludge blended with PS and WAS at a dry mass ratio of 1:1, the groups without Al^{3+} dosing and with low Al^{3+} dosing exhibited similar VSR and CH_4 yield, indicating a low Al^{3+} dose shown in Table 5.1 did not affect anaerobic digestion (Figure 5.5a). Hence, it can be concluded that the Al^{3+} dose required to produce PS with a 1:1 dry mass ratio to WAS does not affect the AD performance. In contrast, increasing the Al^{3+} dose from low to high dramatically decreased VSR and CH_4 yield from 45% to 32% and 0.26 to 0.17 L g^{-1} VS fed (Figure 5.5a). Interestingly, increasing the PS-to-WAS blending ratio from 1:1 to 3:1 mitigated this negative effect of high Al^{3+} dose (Figure 5.5a).

To evaluate the sludge blending effect, results from PS only and WAS only groups were used as baselines to benchmark against values from blended sludge to calculate ΔVSR and ΔCH_4 yield, which are plotted in Figure 5.5b. As can be seen, high Al^{3+} doses did negatively impact both ΔVSR and ΔCH_4 yield (Figure 5.5b). At 1:1 blending ratio, a high Al^{3+} dose can decrease ΔVSR and ΔCH_4 yield for 30% and 32%, respectively (Figure 5.5b). By increasing this ratio to 3:1, ΔVSR and ΔCH_4 losses can be mitigated to 7% and 6%, respectively. This is probably because Al^{3+} had less effect on PS than on WAS. As a matter of fact, the chemical binding between Al^{3+} and proteins has been recognized as a primary contributor to the adverse effects of Al^{3+} on sludge digestibility (Luo et al., 2022).

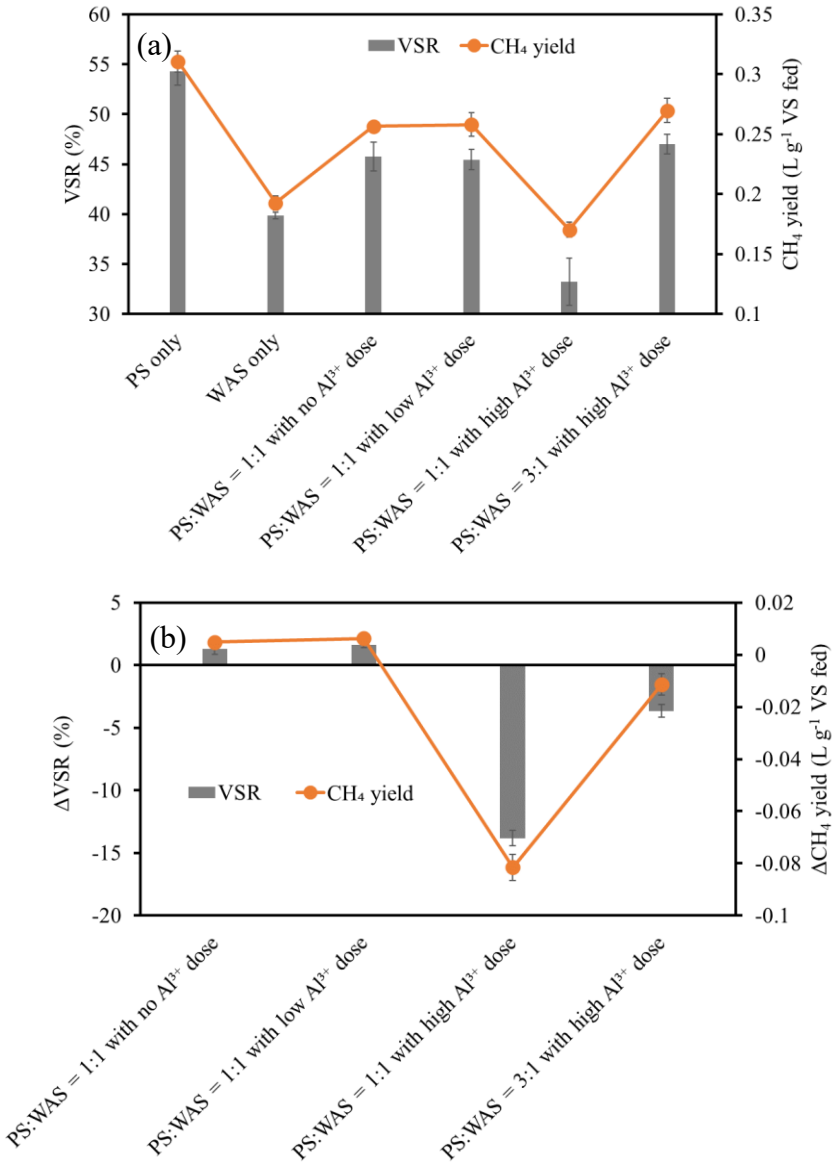

Figure 5.5. (a) VSR and CH_4 yield of all experimental groups; (b) ΔVSR and ΔCH_4 yield of four blended groups.

5.5.3 Effects of blending ratio and Al^{3+} dosing on sludge dewaterability and OP

Dewaterability is an important digestate characteristic because it determines the final cake dryness for economical sludge disposal. As shown in Figure 5.6a, the CST of AD effluent tended to decrease with the increase of Al^{3+} doses, indicating that Al^{3+} dosing improved the blended sludge dewaterability. As a matter of fact, the improvement of digestate dewaterability as a result of Al^{3+}-based coagulant addition has been broadly reported (Jing et al., 1999; Luo et al., 2022; Zhang et al., 2014b). The enhancement of the dewaterability was explained by the interaction between Al3+ and extracellular polymeric substances (EPSs), i.e., the structure of water holding EPSs can be compressed as a result of surface charge neutralization and adsorption by Al^{3+} ions (Barber, 2016; Luo et al., 2022). Moreover, Al^{3+}- based coagulants also act as skeleton builders during sludge dewatering, i.e., the precipitates formed as a result of the binding can create a rigid structure around sludge flocs, transmitting the mechanical dewatering stress through the filter cake (Luo et al., 2022). In addition, since PS usually possess a better dewaterability than WAS (Higgins et al., 2017), it is reasonable to see an high PS blending ratio is expected to result in a better sludge dewaterability (Figure 5.6a).

OP also decreased with the increase in Al^{3+} addition in the blended groups (Figure 5.6b). This can be explained by the precipitation between the OP and Al^{3+} (Zhang et al., 2019a). Previous study reported that OP removal by inorganic coagulants addition improved sludge dewaterability (Zhang et al., 2019a). An explanation was that the precipitates formed by the binding between Al^{3+} and OP can create a rigid permeable lattice structure that maintains high sludge structural strength and in turn impedes compression. Thus, the porous structure of the precipitate may sever as a draining media for dewatering (Luo et al., 2022; Zhang et al., 2019a). Moreover, the improved sludge dewaterability as a result of OP removal can also be explained by the competition between OP and negatively charged sludge particles for cationic polymer (Zhang et al., 2019a). The reduced OP concentration will ideally left more binding sites available on the cationic polymers for neutralizing and flocculating sludge particles (Zhang et al., 2019a). Thus, the negligible OP levels in the two blended groups with high Al^{3+} addition indicates the improvement of sludge dewaterability in this study (Figure 5.6b). It should be noted that OP concentration in WAS is

almost three times that in PS (Figure 5.6b), probably due to the unintended biological phosphorus removal.

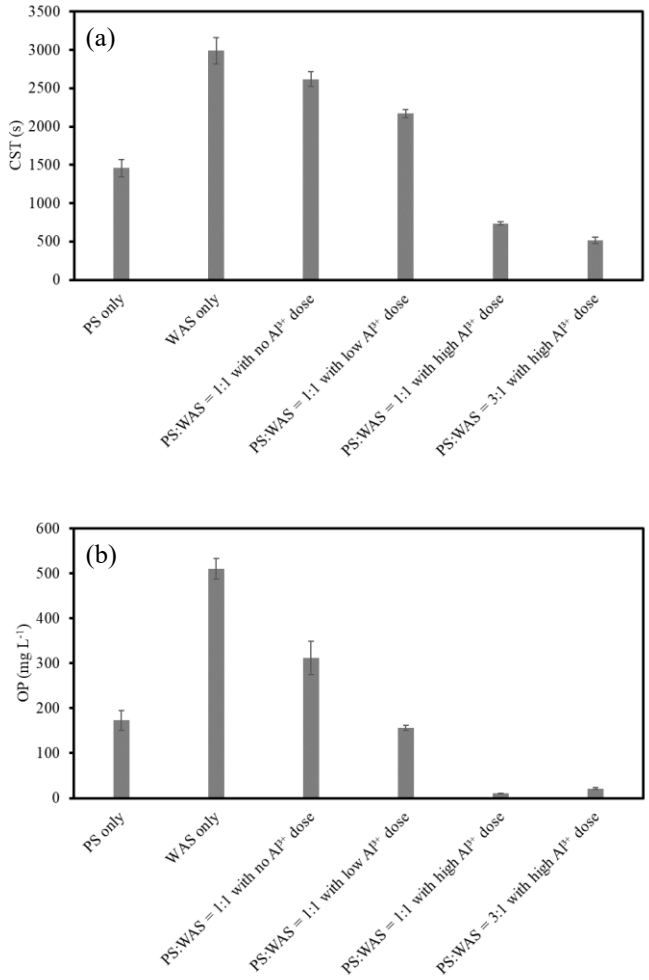

Figure 5.6. Steady-state (a) CST and (b) OP of four blended groups of AD effluent.

5.5.4 Effects of blending ratio and Al^{3+} dosing on TAN and DON production

The remarkably higher nitrogen content in WAS over PS led to the same differences in TAN and DON production (Figure 5.7 a and b). Compared to the baseline average of PS only and WAS only, blending the two in 1:1 ratio with no or low Al^{3+} dose resulted in an average TAN level but a much greater than average DON level (Figure 5.7 a and b). The higher-than-average DON levels in

blended sludges have to do with the Maillard reaction between the reducing sugar hydrolyzed from PS and amino acids hydrolyzed from WAS, which will be elaborated in a later section. It is interesting to observe that high Al^{3+} doses substantially reduced both TAN and DON levels regardless of the blending ratios used (Figure 5.7 a and b), which indicates that high Al^{3+} must have resulted in less available protein for the TAN and DON production. The precipitation of DON by Al^{3+} as indicated in a previous study may further explain the even lower DON levels under high Al^{3+} doses (Zhang et al., 2020b).

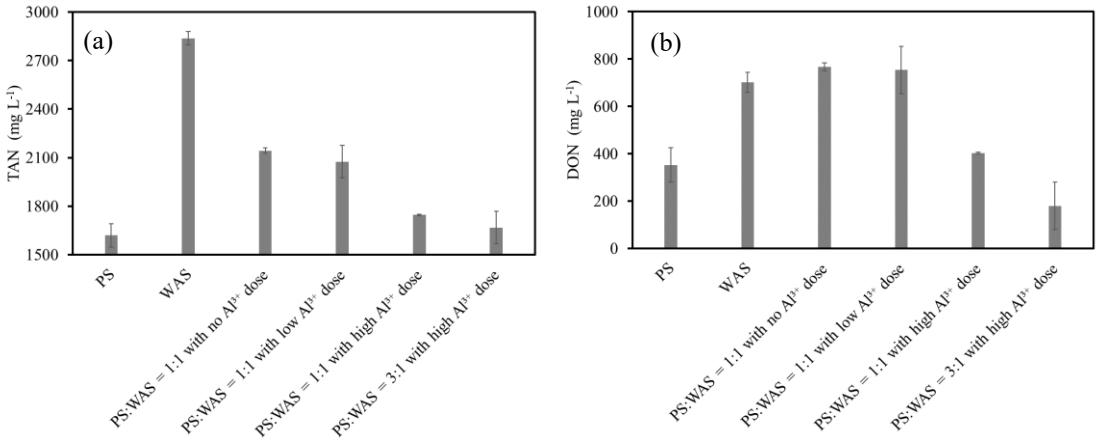

Figure 5.7. (a) TAN and (b) DON concentrations of all experimental groups at steady state.

5.5.5 Effects of blending ratio and Al^{3+} dosing on rDON formation

The centrates from four groups of digestates were subjected to rDON test to understand the effects of sludge blending and Al^{3+} addition on rDON formation during THP. As can be seen in Figure 5.8a, after 5 days of air stripping, the TAN concentrations of all four centrates became lower than 200 mg L^{-1}. After that, all centrates were diluted two times to prevent nitrification from centrate inhibition. With 14 days of aeration, all remaining TAN gradually decreased to undetectable level as a result of nitrification (Figure 5.8b). This can also be confirmed by the corresponding NO_3^--N profiles in Figure 5.8c. Meanwhile, a graduate decrease in DON was also observed because the biodegradable fraction of DON was metabolized into TAN and then nitrate (Figure 5.8d). For WAS only group and the blended group without Al^{3+} addition, their centrate TAN levels stopped

dropping during day 7 and 11. A close inspection revealed that a considerable amount of activated sludge has stuck to and accumulated on the inter wall of these glass jars above the water surface as a result of mixing, which must have compromised sludge activity in the mixed liquor. This problem was corrected by spiking 0.05 g mL^{-1} thickened activated sludge in each bottle on the 12^{th} day, and thereafter all glass jars were manually shaken on a daily basis to keep all biomass in the mixed liquid. As shown in Figure 5.8 b and c, as soon as the new inoculum was added, both groups TAN levels quickly dropped to undetectable concentrations, correspondingly to which, nitrate concentrations dramatically increased. In contrast, the control group produced negligible amount of TAN and DON during the 14 days of aerobic treatment.

The final rDON concentrations in centrates from four groups were summarized in Figure 5.8e. As can be seen, the rDON in the blended group without Al^{3+} addition was 19% higher than that of the average of the two individual PS only and WAS only groups. Again, this was hypothesized because rDON is a product from Maillard reaction between carbohydrate rich in PS hydrolysate and amino acids rich in WAS hydrolysate. Thus, it is confirmed that PS and WAS blending can substantially increase the rDON formation in THP. Hence, separating PS from WAS in the course of THP could be taken advantage of as an effective means to control rDON. Furthermore, with high Al^{3+} addition, the rDON concentration in the blended mixture was 50% lower than that without Al^{3+} addition (Figure 5.8e), indicating rDON precipitation by Al^{3+}. Therefore, Al^{3+} addition could be taken advantage of as another effective means to control rDON.

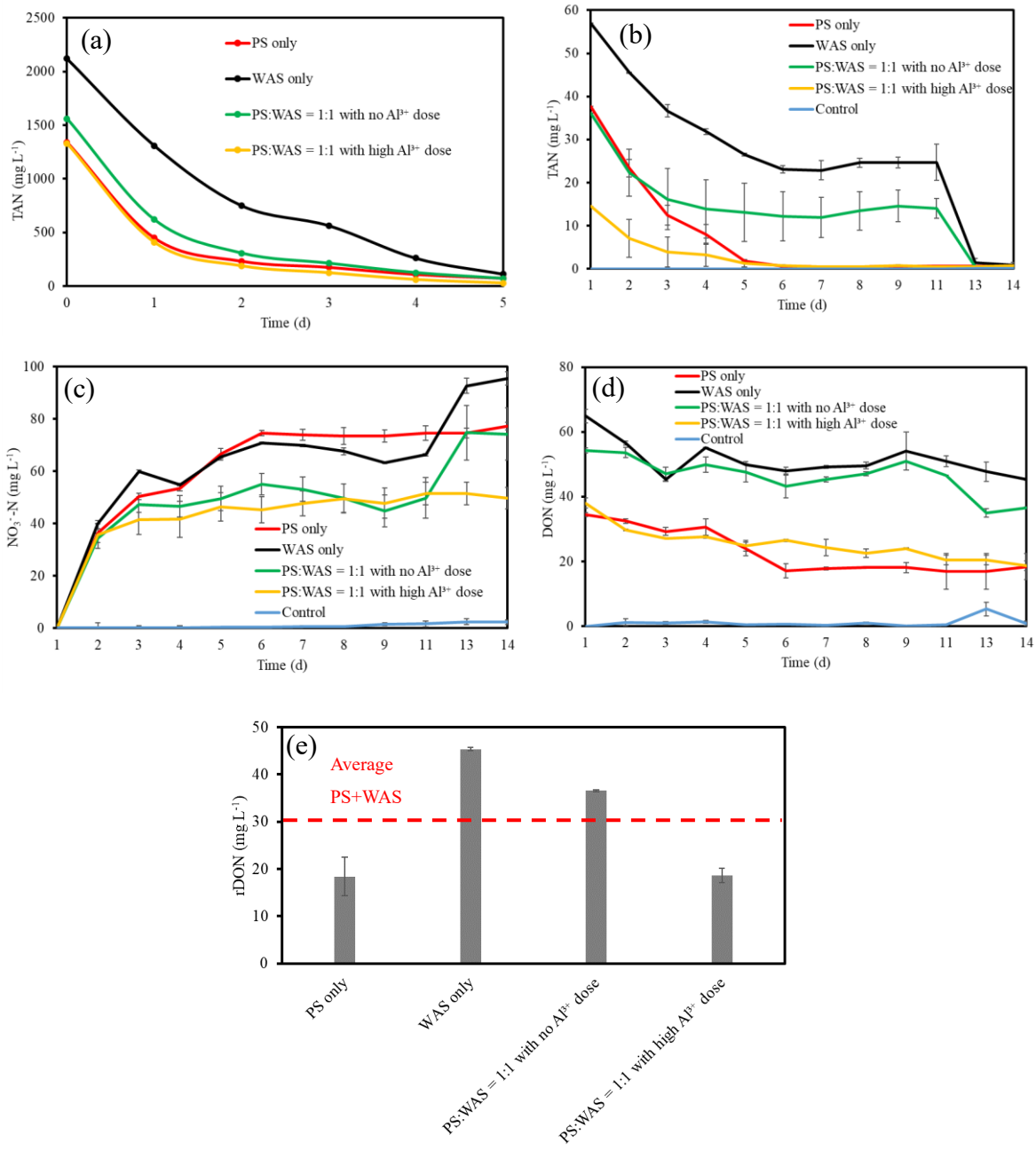

Figure 5.8. (a) TAN profiles in four experimental groups over five days of air stripping; (b) TAN, (c) NO_3-N, and (d) DON concentration profiles for 14 days of aerobic incubation; and (e) final rDON in four AD centrates after aerobic incubation.

5.6 Discussion

5.6.1 Pros and Cons of CEPT-enabled carbon diversion

To redirect wastewater organic carbon to anaerobic digesters via PS production through the most popular CEPT method, coagulants such as alum needs to be employed. Results in Figure 5.5 exhibited that only high Al^{3+} doses may bring negatively impact on the sludge digestibility. It is usually believed that this adverse effect is from Al^{3+} binding with WAS protein but not the toxicity of Al^{3+} (Gossett et al., 1978; Kim and Chung, 2015). As we know, PS usually contains less protein but more carbohydrates than WAS (Tezel et al., 2011). Therefore, blending more PS as shown in Figure 5.5 was able to mitigate the problem to a great extent by reducing the protein content in the blended sludge so as to minimize the unavailability of protein for bacterial degradation. Although THP might have broken down the binding between Al^{3+} and proteins, the binding between these two might just resumed in the subsequent AD. Moreover, adding Al^{3+} also improved sludge dewaterability as indicated by the much lower CST value of the digestate (Figure 5.6a). OP precipitation by Al^{3+} is presumed to be the reason behind. This is because these precipitates are known to form skeleton builders in aid of water drainage through the sludge cake (Luo et al., 2022). In addition, precipitation also reduced the competition of OP with negatively charged sludge particles for cationic polymer (Zhang et al., 2019a).

Although THP is commonly used for enhancing sludge digestibility, blending PS with WAS has been shown in this study to lead to excessive rDON production, which is not the case when WAS only or PS only was pretreated (Figure 5.8e). This is because PS rich in carbohydrates and WAS rich in proteins provided precursors of reducing sugar and amino acids required for Maillard reaction in THP (Zhang et al., 2021a; Zhang et al., 2020b). Fortunately, a high Al^{3+} dose was able to precipitate rDON and attenuated its concentration from 38 to 19 mg L^{-1}. As a matter of fact, adding metallic ions such as Al^{3+} has been proposed as a strategy to control rDON in previous studies (Gomyo and Horikoshi, 1976; Zhang et al., 2020b). Various mechanisms including chelation and coagulation were involved in the interaction of rDON with metallic ions as reported in previous studies (Rufián-Henares and de la Cueva, 2009; Wang et al., 2011). For example, the

ketone or hydroxyl groups in a primary type of rDON, i.e., melanoidins, can act as an donor groups and participate in the chelation with metals (Rufián-Henares and de la Cueva, 2009). Besides, the chelation of metal ions with amino and carboxyl groups in amino acids or the hydroxyl groups in sugar can also decreased the rate of Maillard reaction (Ramonaitytė et al., 2009). Moreover, high molecular melanoidins in colloidal range with the negative net energy charge can be removed through coagulation by inorganic coagulants such as Al^{3+} (Arimi et al., 2015).

5.6.2 Implication on carbon diversion adoption

PS production through the cost-effective CEPT is a crucial step towards the implementation of carbon diversion. Frist-hand experimental data obtained from this study revealed that there is a trade-off between PS production and energy recovery, i.e., the more carbon is diverted into PS, the higher dose of coagulant is required, which in turn make the mixture of PS and WAS less biodegradable (Figure 5.5). It is actually broadly accepted that Al^{3+} addition can adversely affect the blended sludge anaerobic digestibility (Abbott and Eskicioglu, 2015; Gossett et al., 1978; Luo et al., 2022; Novak and Park, 2010a). Although the implementation of THP may improve the sludge biodegradability, rDON formation due to blending PS with WAS is another side effect that has not been previously taken into consideration of carbon diversion. Many WRRFs such as those in Chesapeake Bay watershed, coastal areas of North Carolina, mid-Colorado and Okanagan Lake area of British Columbia, Canada have a stringent TN requirement, e.g., < 3 mg L^{-1}, because of the potential adverse effects of rDON compounds on biological activity (Zhang et al., 2021a). Therefore, for WRRFs considering adopting the carbon diversion strategy, a comprehensive evaluation of the overall gains is important. This is because energy/carbon neutrality is not the primary responsibility of WRRFs. Instead, their discharge quality and solids reduction efficiency are usually more important considerations. Hence, whether to adopt or to what extent to adopt carbon diversion depends on the priorities of WRRFs and thus should be decided on a case-by-case basis. To assist decision making, a comparison of the three scenarios using data obtained from this study is presented in Figure 5.9. A 0.5 g g^{-1} aerobic growth yield is assumed for WAS production from aeration tank (Wan et al., 2016). Besides, 80% VS content in TS is also assumed. Based on the mass balance, Figure 5.9a shows that without any carbon diversion, namely WAS

only, 55% total solids reduction can be achieved with 50% wastewater organics oxidized in aeration tank and another 19% turned into CH_4 in ADs, respectively (Figure 5.9a). In comparison, diverting carbon into PS produced with dry mass ratio to WAS equal to 1:1 achieved 51% total solids reduction with 33% wastewater organics oxidized in aeration tank and another 31% turned into CH_4 in anaerobic digesters, respectively (Figure 5.9b). In the case of high PS production with dry mass ratio to WAS equal to 3:1, only 48% total solids reduction can be achieved with 20% wastewater organics oxidized in aeration tank and another 41% turned into CH_4 in anaerobic digesters, respectively (Figure 5.9c). A pattern can be seen is that, as the PS-to-WAS blending ratio increased from 0:1 to 1:1 and 3:1, the final residual TS increased 9% and 16%, respectively. The aeration electricity can be reduced by 35% and 60%, respectively. The CH_4 energy recovery can be increased for 67% and 120%, respectively. Apparently, the extents of energy savings and recovery are both substantially greater than that of the residual solids increase. Therefore, a comprehensive technoeconomic analysis is needed for decision making down the road to take into account the increased biosolids disposal cost, the PS clarifier installation capital, CEPT operational cost, secondary capacity upgrading saving, as well as the energy bill savings. Very importantly, the cost of activated carbon for rDON removal should be also taken into consideration if the room for accommodating the effluent permissible TN level is limited. Previous study reported that the cost of the biosolids treatment can be as high as 40-50% of total wastewater treatment operational costs in the U.S. (Turovskiy and Mathai, 2006). Discretion has to be used when it comes to the infrastructural upgrading to carbon diversion design.

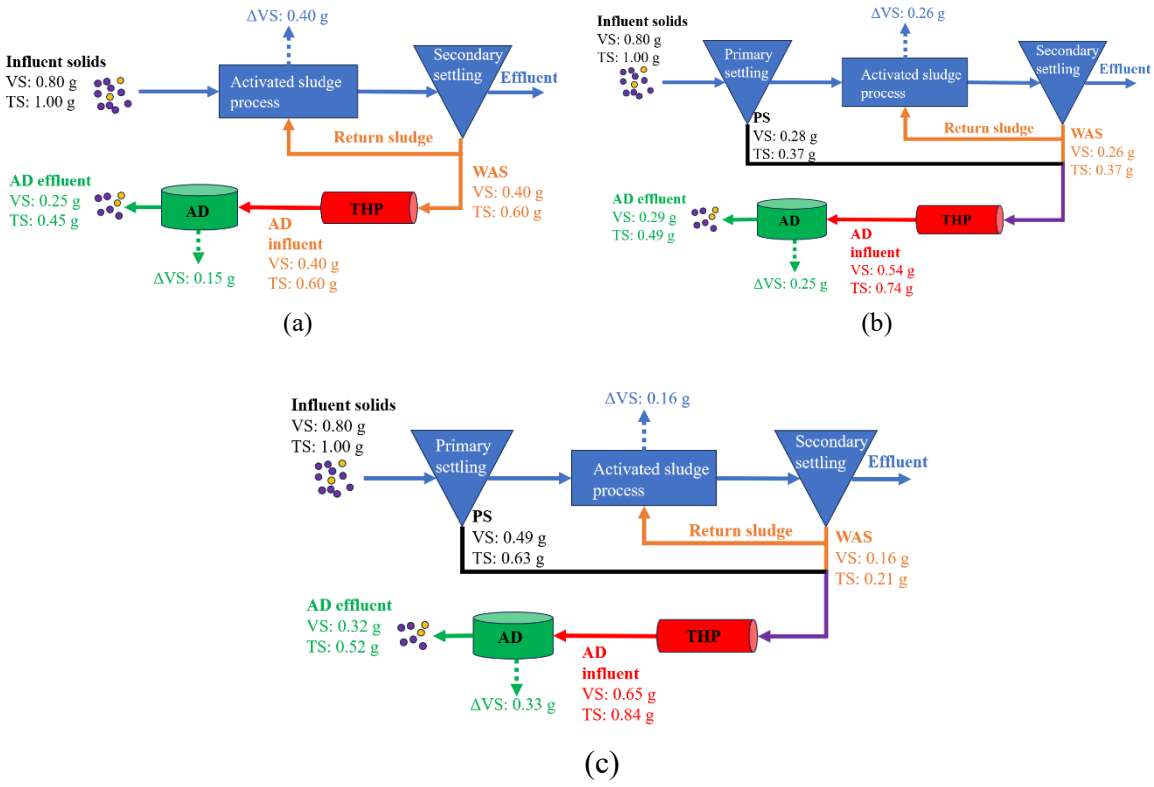

Figure 5.9. Solids mass flow through the WRRF (a) without primary settling, (b) with primary settling and a PS-to-WAS ratio of 1:1, and (c) with primary settling and a PS-to-WAS ratio of 3:1.

5.7 Conclusions

Following concluding remarks can be drawn from this study:

1. Increasing the PS production and blending can on one hand bring greater extents of energy recovery and savings but on the other hand lead to extra residual solids production.
2. Although coagulant addition through CEPT can deteriorate the sludge digestibility, increasing the PS:WAS blending ratio can mitigate the problem.
3. When THP is used as a pretreatment method, blending PS with WAS can result in the formation of excessive rDON which meanwhile can be removed by Al^{3+} dosing.
4. High Al^{3+} doses used for PS production can also improve sludge dewaterability by removing OP.

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Chapter 6 Understanding the effect of a secondary thermal hydrolysis on municipal sludge anaerobic digestion

(This chapter manuscript has been prepared and will be submitted to "Bioresource Technology")

6.1 Abstract

Thermal hydrolysis (TH) has been full-scale implemented as a pretreatment means to expedite the rate of municipal sludge anaerobic digestion (AD). However, a high concentration of soluble chemical oxygen demand (sCOD) usually remains in the TH-AD digestate. It is generally unknown how much methane potential remains after this primary TH-AD treatment, and whether a secondary TH can further improve the sludge methane yield and volatile solid reduction (VSR). In this study, a biological methane potential (BMP) test was performed on digestates collected from three pilot-scale TH-AD systems operated with solids retention time (SRTs) of 10, 12.5, and 15 days to quantify and exhaust their residual BMP, respectively. Subsequently, the three sludges were processed in a secondary TH and then went through another round of BMP test to determine whether new BMP can be created. Results showed that a secondary TH was able to add another 0.09-0.12 L CH_4 g^{-1} VS_{fed} and 9-12% sCOD formation but did not increase VSR. The secondary TH also created an alkaline environment conducive to the mitigation of recalcitrant sCOD formation; however, it did not improve the biodegradability of those recalcitrant sCOD formed in primary TH. The mechanism behind the new BMP creation during the secondary TH is also discussed.

6.2 Keywords

TH, Anaerobic digestion, BMP, sCOD

6.3 Introduction

Thermal hydrolysis (TH) pretreatment has been commercially applied in water resource recovery facilities (WRRFs) for over 20 years for the capacity enhancement of anaerobic digesters (ADs) (Barber, 2016). Many advantages of TH have been reported, which include the improvement of sludge digestibility, dewaterability, pumpability, as well as pathogen, odor, and foam reduction (Abu-Orf and Goss, 2012; Barber, 2016; Higgins et al., 2011). TH used in WRRFs is usually operated between 160 and 180 ˚C under a pressure about 6 bars for 20 to 30 minutes (Barber, 2016). In the course of TH, high temperature and pressure result in the rupture of activated sludge cell walls, the destruction of their extracellular polymeric substances, and in turn the reduction of the sludge viscosity and recalcitrancy (Barber, 2016; Bougrier et al., 2006). This TH pretreatment thus can upgrade the treatment capacity of existing ADs by shortening their sludge retention time (SRTs) from 25-30 days to 15 days or less even when the sludge as thick as total solids (TS) $\geq$ 9% was fed (Choi et al., 2018; Donoso-Bravo et al., 2011).

However, it is also broadly reported that the effluent from TH-AD usually contains remarkably high levels of soluble chemical oxygen demand (sCOD) (Yan et al., 2022). For example, sCOD in full-scale TH-AD operated in the U.S. can be as high as 3583 mg L^{-1} sCOD, while the conventional ADs only produced 300 mg L^{-1} sCOD (Zhang et al., 2016). Likewise, the full-scale TH-AD operated in Austria produced 5700 mg L^{-1} sCOD compared to only 900 mg L^{-1} sCOD when TH was not used (Phothilangka et al., 2008). The role of TH has been controversial because it on one hand solubilizes volatile solids into sCOD for improved biochemical methane potential (BMP), and on the other hand it produces recalcitrant dissolved organic matters via Maillard reaction (Zhang et al., 2021a).

Hence, such a high sCOD remaining in the TH-AD digestate warrants further understanding on:

(i) how much biochemical methane potential (BMP) remains in the digestate; and

(ii) whether a secondary TH can further improve the digestate BMP.

To this end, this study first run TH-AD digestates produced from ADs operated with SRTs of 10, 12.5, and 15 days through BMP tests to measure their residual BMPs. After that, these digestates were subjected to a secondary TH to determine whether additional BMP can be created. The mass flow of various subcomponents of total COD (tCOD), total Kjeldahl nitrogen (TKN), and total solids (TS) through each treatment step was tracked and analyzed for better understanding the role of a secondary TH at play.

6.4 Materials and Methods

6.4.1 Experimental design

Dewatered cake with 30% TS was collected from Arlington Water Pollution Control Plant in Arlington, Virginia. This cake was made from primary sludge and waste activated sludge blended with a ratio of 3:2 (v/v) and then diluted to 16% TS with deionized water prior to treatment in a primary TH. The TH effluent was subsequently fed into three mesophilic ADs. The AD effluent was treated in a primary BMP test to measure and exhaust its residual BMP. After that, the BMP sludge was treated in a secondary TH and then went through a secondary BMP test to check if any new BMP can be created or sCOD can be removed. The specific procedure in each step is described in detail below.

6.4.2 TH setup

A 5-liter TH system used for this study was manufactured by CAMBI™ (Figure 6.1 left). The sludge was fed from the inlet tray at the top of the TH unit into the reactor tank. The steam from the steam generator was injected into the reactor to quickly heat the sludge to 165 ˚C at 6 bars. After 30 min, the steam treated sludge was ejected through an orifice into a flash tank beneath the reactor (Figure 6.1 left). The treated sludge was then cooled down to room temperature prior to subsequent AD or BMP treatments.

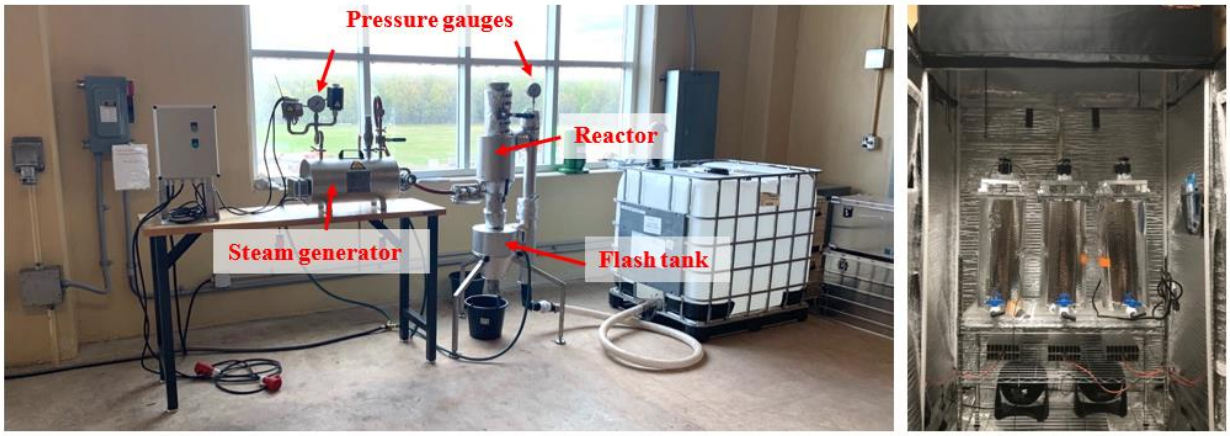

Figure 6.1 *left*: CAMBI™ TH setup; *right*: three mechanically mixed ADs in a temperature-controlled space.

6.4.3 AD setup

Three units of mechanically mixed ADs with 10 L working volume and 5 L headspace in each are as shown in Figure 6.1 right. They were operated in parallel in a space with temperature controlled at 36.5 ± 0.3 ˚C. These ADs were inoculated with digestate collected from a full-scale TH-AD operated by the Blue Plains Advanced Water Treatment Plant in Washington, DC. The 16% TS sludge produced from TH was diluted to 9% with deionized water and then fed into each AD. The SRTs of the three ADs were controlled at 10, 12.5, and 15 days, respectively. Before this experiment, the three ADs had been operated for 190 days and reached steady state.

6.4.4 BMP test

A 16-channel aerobic/anaerobic respirometer system (AER-800, Challenge Technology, Louisville, CO) was used to perform BMP tests with a triplicate design for each sample. The primary BMP test was performed without inoculation because the samples were fresh digestate from TH-ADs in Figure 6.1. After that, BMP triplicate samples were combined and then treated with a secondary

TH prior to a secondary BMP test in which each group of sludge was split into triplicate again and inoculated with digestate collected from the Blue Plains Advanced Water Treatment Plant at a substrate-to-inoculum ratio of 3:2 (v/v). Blank bottles containing only inoculum were prepared for deducting background methane production from inoculum. Control bottles in which inoculum was fed with glucose were also added for checking the inoculum activity.

All respirometer bottles were placed in an incubator shaker operated at 70 rpm with temperature controlled at 36.5 °C. The CO_2 and H_2S contents in biogas produced from each bottle were scrubbed by inline potassium hydroxide scrubbers. The remaining biogas was regarded as methane and quantified by a bubble counter in each respirometer channel. The methane production from each bottle was real-time monitored throughout the BMP test until each methane accumulation profile reached a plateau.

6.4.5 Chemical analysis

The concentrations of COD, TKN, and total ammonia nitrogen (TAN) were determined using Hach test kits of TNT 822, TNT 880, and TNT 832, respectively (Hach, Loveland, CO). Samples for soluble substances measurement including sCOD, soluble TKN (sTKN), and TAN were passed through 0.45 μm nylon filters (Aura Industries, New York, NY). The dissolved organic nitrogen (DON) concentration was calculated as the difference between sTKN and TAN. pCOD was calculated as the difference between tCOD and sCOD. Particulate nitrogen (pN) was calculated as the difference between TKN and sTKN. Meanwhile, pH and alkalinity were measured with an automatic potentiometric titrator (HI901C, HANNA, Woonsocket, Rhode Island). TS and volatile solids (VS) were measured according to standard methods (APHA, 2012). Their difference was calculated as the inorganic solids (IS). Besides, the biogas production rate during anaerobic digestion was real-time monitored using calibrated tipping-bucket meters (Archae Press, Nashville, USA) coupled with automatic data loggers (MicroDAQ, Contoocook, NH). Moreover, biogas methane was measured using a gas chromatography equipped with a thermal conductivity detector (GC-2014, Shimadzu, Columbia, MD).

6.4.6 Data analysis

T-tests were performed to assess whether statistical differences can be found in the daily biogas production rates for the three ADs as a means to confirm steady states have been reached. Then, the steady-state data were collected on a weekly basis for at least four times and presented as the mean values with standard errors. Likewise, all replicate data from BMP tests were also presented as the mean values with standard errors. The sample ash contents were used as an internal control for mass balance calculation by virtue of their conservative nature.

6.5 Results

6.5.1 Effect of SRTs on TH-AD performance

Although the TH-AD technology has been broadly applied, whether a shorter than 15-day SRT can be used for its AD unit has rarely been studied. Figure 6.2a shows that the steady state volatile solids reduction (VSR) proportionally decreased from 60.7% to 53.7% along with the SRT decrease from 15-day to 10-day, indicating that the extent of solids reduction was limited by SRTs. Accordingly, residual sCOD in AD effluent increased from 6900 to 7153 mg L^{-1} along with the SRT decrease (Figure 6.2a). This inverse relationship between VSR and sCOD suggests that methanogenesis might have been the rate-limiting step in ADs operated with lower SRTs (Ma et al., 2013). Consequently, the methane yield at SRT of 15 days was slightly higher than those at SRTs of 10 and 12.5 days (Figure 6.2b). Regardless, residual sCOD in all three TH-ADs were above 6900 mg L^{-1} which is significantly greater than the typical values reported in conventional AD (Xue et al., 2015; Zhang et al., 2016).

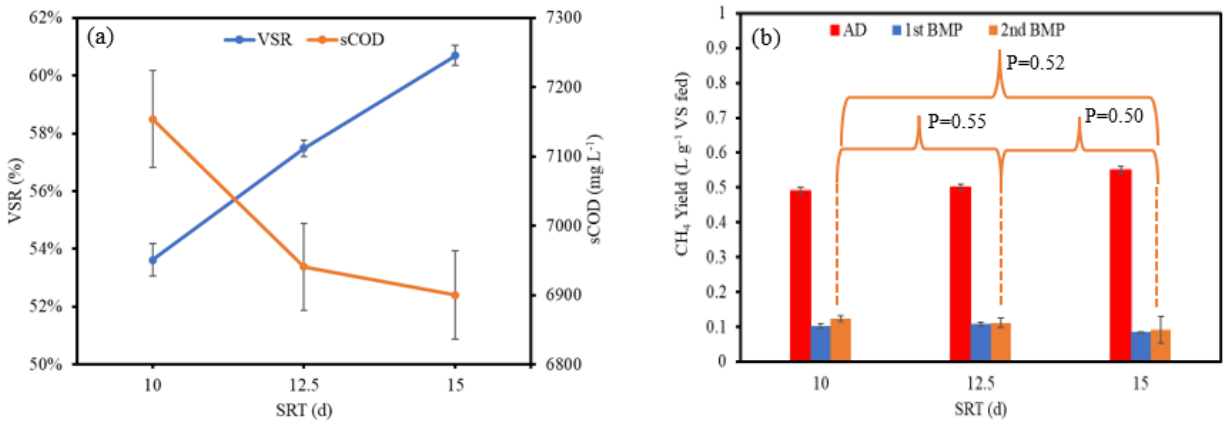

Figure 6.2. (a) Steady state VSR and sCOD of ADs operated under three SRTs; (b) Methane yield during AD and two rounds of BMP tests.

6.5.2 BMP before and after the secondary TH

The BMP profiles of the digestates produced at SRTs of 10, 12.5, and 15 days before and after the secondary TH are shown in Figure 6.3 a and b, respectively. As can be seen, the difference among the three sludges' BMP profiles was insignificant. But the ramp rates of BMP profiles before and after the secondary TH were very different. Specifically, it took over 25 days to exhaust BMP remaining in TH-AD digestates (Figure 6.3a); however, it only took a third of the time (only 6 days) to exhaust the BMP recreated after the secondary TH (Figure 6.3b). The residual BMP in TH-AD digestate was 16-21% that produced in AD, which is slightly lower than the additional BMP created after secondary TH (Figure 5.2b). T-test results in Figure 6.2b revealed that the difference in BMP recreated after the secondary TH was insignificant ($P > 0.05$) among the three SRTs' sludges probably because the primary BMP has exhausted and wiped out their characteristics differences.

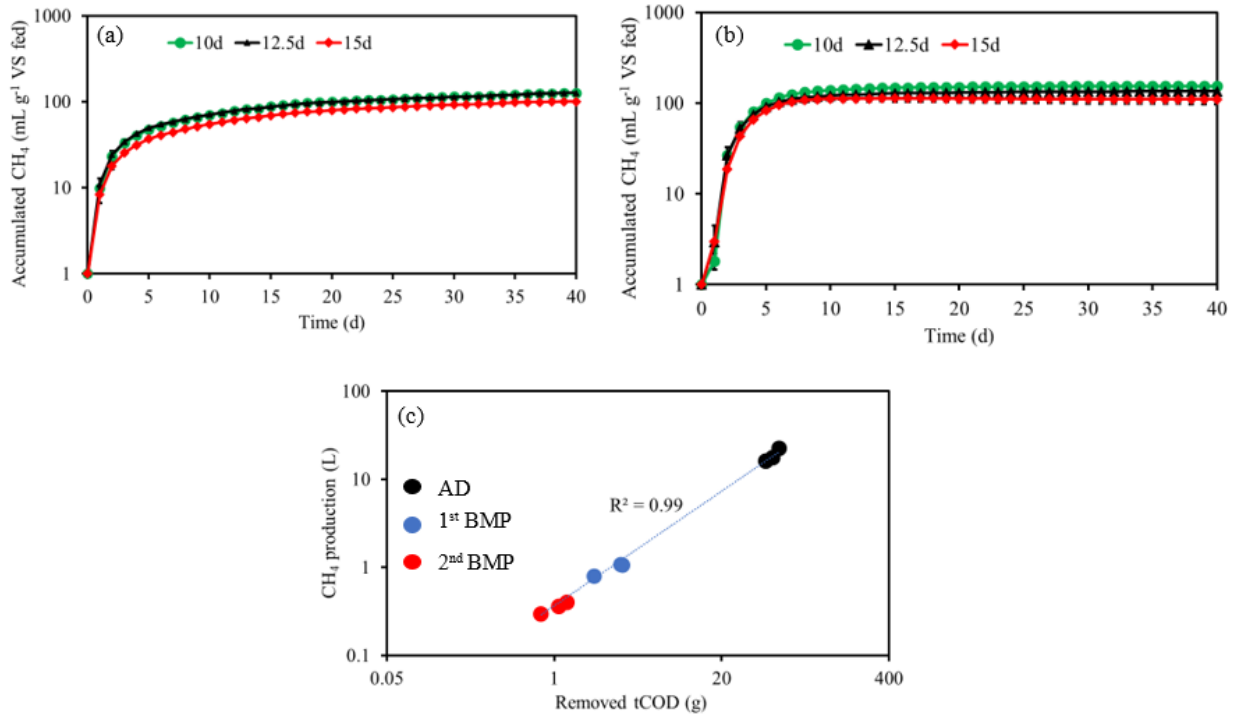

Figure 6.3. Methane accumulation during the (a) primary and (b) secondary BMP; (c) A crosscheck of methane production data with the tCOD removal data

6.5.3 Crosscheck methane production results

In order to crosscheck the accuracy of all methane measurement results, the methane production data were plotted against the tCOD removal results obtained from all AD and BMP treatments. Figure 6.3c shows a linear correlation ($R^2 = 0.99$) with a slope of 0.36 L CH_4 g^{-1} tCOD between the two individual sets of data. This value is very close to the theoretical value of 0.35 L CH_4 g^{-1} tCOD assuming biogas production is the only outlet for COD to leave the closed system of AD and BMP (Van Lier et al., 2008).

6.5.4 COD turnover

Since the primary role of TH is to break down pCOD into sCOD (Barber, 2016), and the methane production during AD or BMP is theoretically the only system outlet responsible for tCOD change, the turnover of tCOD, pCOD, and sCOD in the course of all treatments in this study is plotted in Figure 6.4. In general, the digestates produced from three different SRTs followed the same trend. First, the primary TH turned around 22% tCOD in the form of pCOD into sCOD with minor tCOD change probably due to the volatilization occurred when sludge coming out of the TH flash tank (Figure 6.4a). It should be noted that this flash tank volatilization is an artifact in the pilot TH system shown in Figure 6.1 *left* because the full-scale TH system is physically integrated with AD in a closed system without an outlet for volatile compounds to escape TH. Following TH, AD turned 13-14% tCOD in the form of sCOD and 28-35% tCOD in the form of pCOD into methane, leading to 41-49% tCOD destruction. There was still about 8-10% tCOD in the form of sCOD remaining at the end of the AD with levels ranging from 6900 to 7100 mg L^{-1} as shown in Figure 6.2a. In the next 40 days of primary BMP testing, the levels of these sCOD did not show substantial changes, indicating they are recalcitrant sCOD under anaerobic condition. In contrast, it was mainly the 9-14% tCOD in the form of pCOD that was degraded and converted to methane during the primary BMP (Figure 6.4). The following secondary TH again hydrolyzed another 18-22% tCOD in the form of pCOD into sCOD. Interestingly, there were 8-11% tCOD loss during the secondary TH, which was greater than that in the primary TH. The high pH and potential volatile pyrazine formation might be the reason. As shown in Figure 6.5a, a major difference between the primary and secondary TH lies in their pH environment. Although the primary TH resulted in an acidic pH as low as 5.6, pH peaked at 9.2 in the secondary TH. This pH difference can be attributed to the disparate characteristics between raw and digested sludge. Specifically, raw sludge contained more readily biodegradable organic matter which was degraded and partially acidified during the primary TH, while the production of the alkaline compounds such as TAN was very limited (Figure 6.5b). In contrast, most of the easily biodegradable organics have been depleted in digested sludge, especially after the primary BMP, resulting in a high alkalinity concentration (Figure 6.5 b and c) during the secodnary TH. Meanwhile, the effect of decarbonation in flash tank might have also further contributed to the pH increase in secondary TH. Similar phenomena were also reported in other studies (Takashima, 2008; Yang et al., 2019b). Consequently, TAN fed into

TH also peaked at 1870-2130 mg L^{-1} (Figure 6b). It is known that ammonia competes with the precursors of Maillard reaction for pyrazine formation (Chen et al., 2000). This reaction is catalyzed by basic environment, e.g., pH 9 (Yu et al., 2012). The TH environment has been proven to be conducive to Maillard reaction (Zhang et al., 2021a; Zhang et al., 2020b) and thus might have provided an ideal environment for pyrazine formation. Pyrazines are monocyclic aromatic rings with two nitrogen atoms in para position (Müller and Rappert, 2010). Due to their low vapor pressure, the pyrazines evaporate easily, especially at high temperature coming out of the flash tank in Figure 6.1 *left*, which explains the substantial tCOD loss during the secondary TH.

The secondary BMP on the other hand only converted sCOD to methane, leaving pCOD untouched (Figure 6.4), implying that the fraction of pCOD that has survived all previous treatments was indeed recalcitrant. Since the primary BMP has exhausted all raw sludge biodegradability, it can be inferred that this new BMP was from the sCOD created during the secondary TH. It should be noted that there was still around 2700-2880 mg L^{-1} sCOD remaining after the secondary BMP, which is actually not much different from the sCOD levels remained at the ends of AD and primary BMP. This consistency further indicates that the secondary BMP was provided from the sCOD created during the secondary TH.

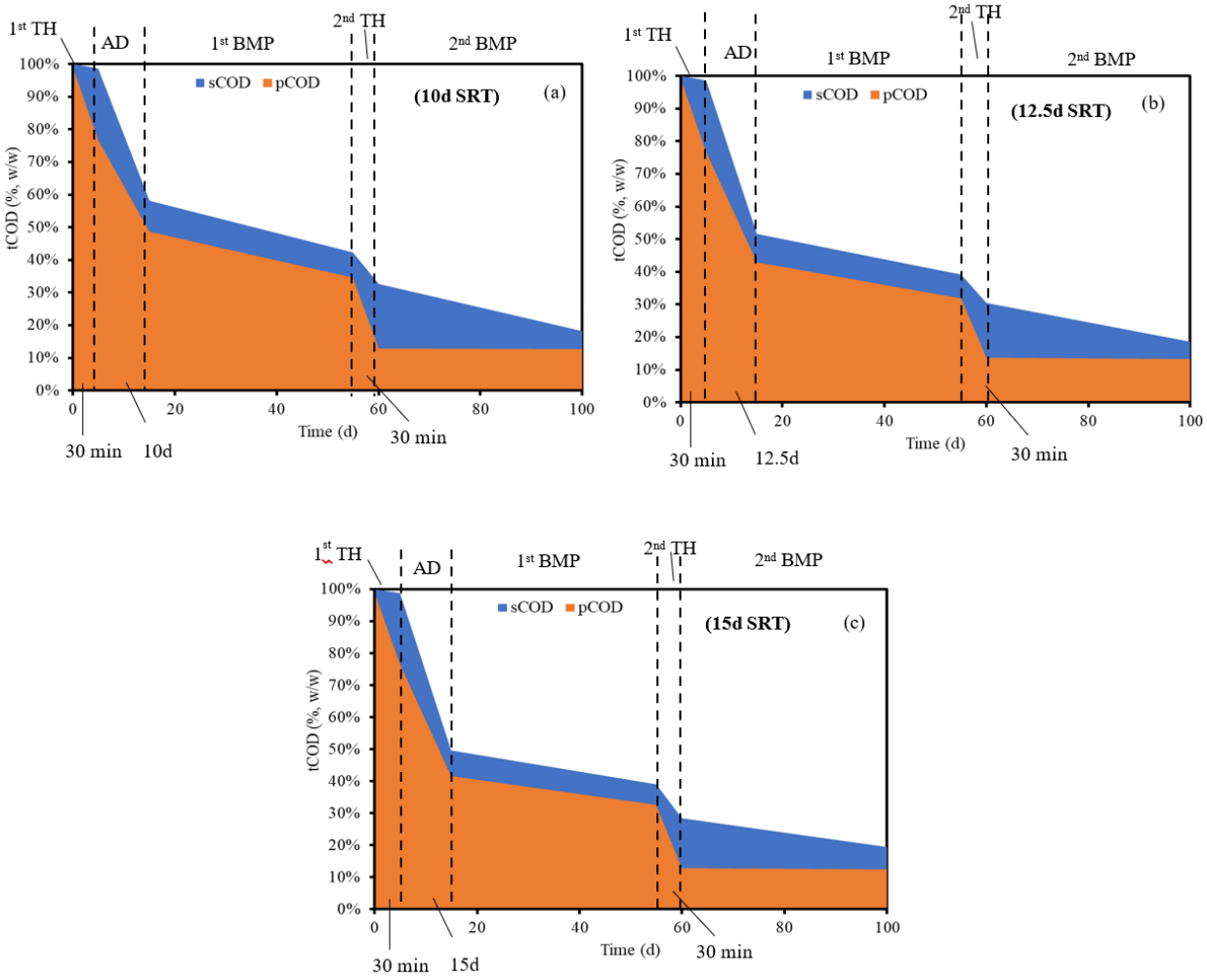

Figure 6.4. tCOD, sCOD, and pCOD turnover in digestates produced from SRTs of (a) 10 days, (b) 12.5 days, and (c) 15 days throughout the TH-AD-BMP-TH-BMP treatments.

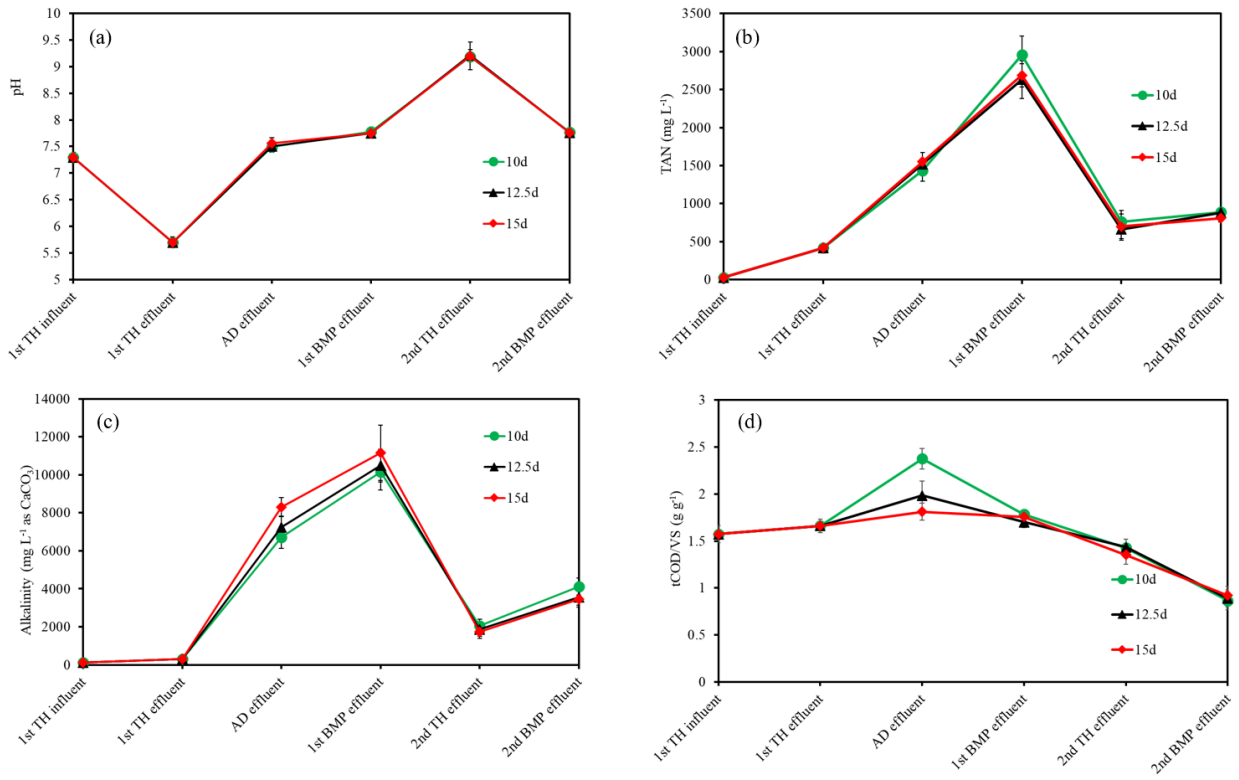

Figure 6.5. Profiles of (a) pH, (b) TAN, (c) Alkalinity, and (d) tCOD/VS of sludge sample in the course of TH-AD-BMP-TH-BMP treatments with AD SRTs of 10d, 12.5d, and 15d.

6.5.5 Nitrogen turnover

Along with the tCOD transformation, a fraction of pN has also been broken down into TAN and DON. Again, very similar nitrogen turnover trends have been observed in all three sludges (Figure 6.6). In general, primary TH hydrolyzed around 50% TKN in the form of pN into DON, leaving 11% TKN in the form of TAN that came with the raw sludge unchanged. Minor TKN was lost during primary TH probably due to volatilization from the flash tank (Figure 6.6). It was the subsequent AD that converted 30-33% TKN in the form of DON into TAN along with another 5-9% TKN in the form of pN hydrolyzed into DON.

During the subsequent 40 days of primary BMP, another 11-16% TKN in the form of pN was hydrolyzed into DON; while TAN level remained almost unchanged during the primary BMP. Different from the COD turnover, more pN removal (e.g., 16% TKN) was achieved in the primary BMP test than that (e.g., 9% TKN) in the AD. This is because the short SRT used in AD actually limited the hydrolysis of pN since protein is usually biodegraded after carbohydrates in AD (Yang et al., 2015). There was about 7-10% TKN loss during primary BMP, which might be due to ammonia volatilization. This is because TAN level has peaked at 2600-3000 mg L^{-1} in the primary BMP as a result of the extensive degradation of pN (Figure 6.5b). Meanwhile, pH has also increased to over 7.5 in all three sludges as a result of the alkalinity increase (Figure 6.5 a and c). These are the favorable conditions for free ammonia formation and stripping alongside the biogas production (Figure 6.6). The pH level even dramatically increased to 9.3 after the secondary TH. This is a common phenomenon observed in TH of biomass that has been exhausted with biodegradability (Takashima, 2008; Yang et al., 2019b). As previously mentioned, this high pH TH environment provides the ideal condition for pyrazine formation from ammonia, which explains a dramatic TAN decrease and a corresponding DON increase in the secondary TH (Figure 6.6). This pyrazine formation also explains why the DON increase was greater than pN destroyed in all three sludges (Figure 6.6).

In the secondary BMP, 18-21% TKN in the form of TAN increased for the biodegradation of DON created during secondary TH, along with which pH dropped to 7.8 and alkalinity increased to around 4000 mg L^{-1} as $CaCO_3$ (Figure 6.5c). It is noteworthy that pN did not change in all three sludges during the secondary BMP, suggesting these solid biomasses are indeed recalcitrant as they have survived a series of TH-AD-BMP-TH-BMP treatments. Likewise, 300-350 mg L^{-1} DON still remained at the end of the 40 days of secondary BMP, which is not much different from the DON remained after AD. Hence, these recalcitrant DON (rDON) was most likely the product of Millard reaction formed during the primary TH as reported in previous studies (Ortega-Martínez et al., 2023; Zhang et al., 2021a). The fact that the same amount of rDON (12% TKN) survived both BMP tests before and after the secondary TH also indicates that the secondary TH did not create new rDON. This can be explained by the competition of Maillard reaction precursors by the peak ammonia level in Figure 6b for the formation volatile pyrazine (Chen et al., 2000).

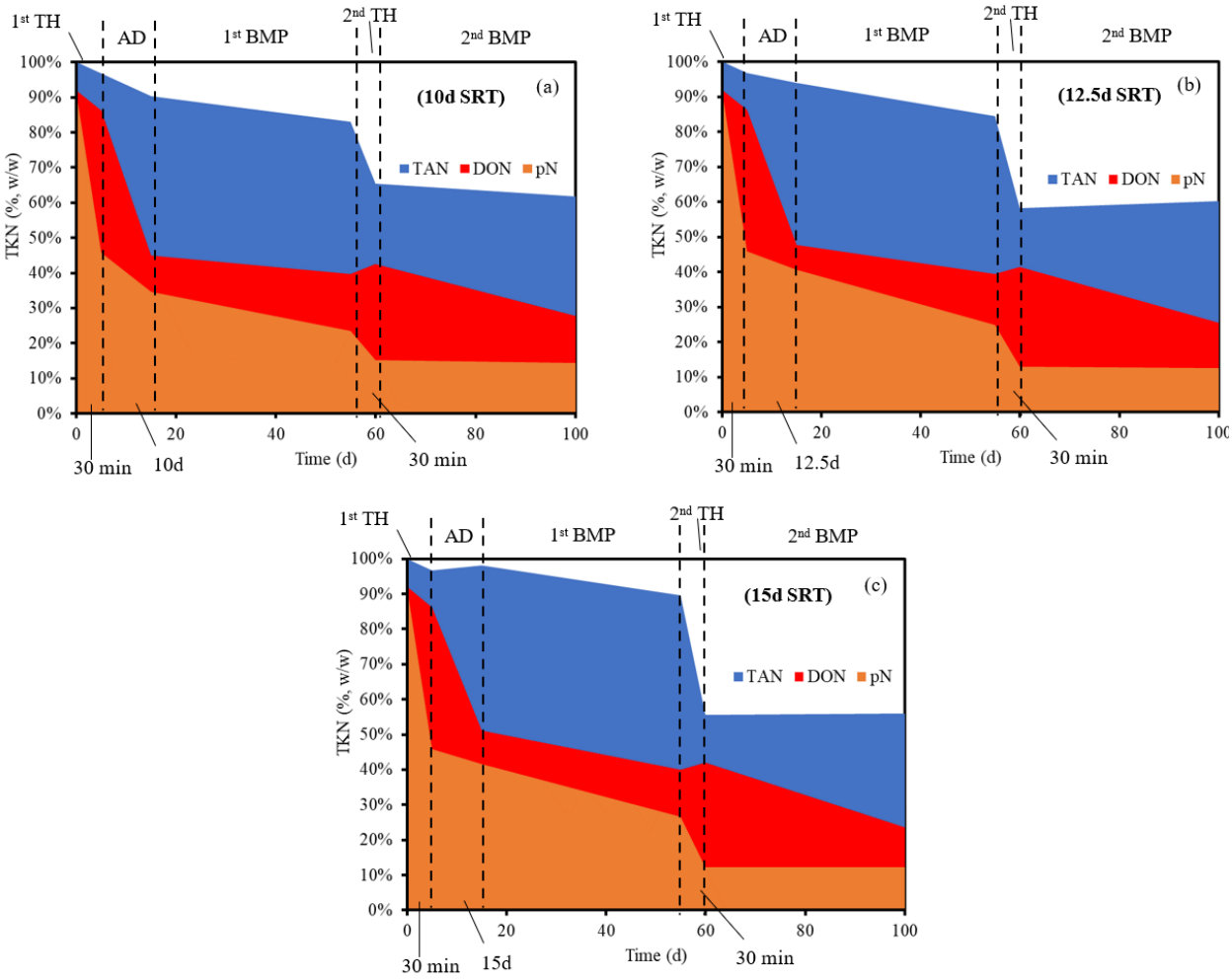

Figure 6.6. TKN, TAN, DON, and pN turnover in digestates produced from SRTs of (a) 10 days, (b) 12.5 days, and (c) 15 days in the course of TH-AD-BMP-TH-BMP treatments

6.5.6 Solids turnover

Solids reduction is a primary goal of TH-AD. Figure 6.7 demonstrates the turnover of TS, VS, and IS. In general, majority of the TS reduction (39-45%) was achieved during AD, which gives a VSR of 54-60% as shown in Figure 6.2a. It is interesting to observe that BMP did not contribute to VSR, especially in the secondary BMP where only sCOD but not pCOD was biodegraded (Figure 6.7). The primary BMP did achieve some VSR (4-9%) left from AD due to the limitation of SRTs at 10 and 12.5 days. At a 15-day SRT, negligible VSR was achieved in the primary BMP, confirming the sufficiency of a 15-day SRT for VSR in a TH-AD setup. In contrast, a secondary TH only contributed < 2.5% VSR. Comparing the tCOD profiles in Figure 6.4 to the VS profiles in Figure 6.7, one may find a pattern, i.e., tCOD removal was greater than VSR, especially after AD. This has to do with sludge composition change over the series of treatments. The organic fraction of municipal sludge mainly consists of lipids, proteins, and carbohydrates. According to previous study, the typical ranges of tCOD/VS ratios in lipids, proteins, and carbohydrates are 2-2.9, 1.4-1.5, and 1.07-1.18, respectively (Ahnert et al., 2021). A plot of tCOD/VS ratio profiles in Figure 6.5d revealed that the sludge came with a tCOD/VS ratio of 1.6, which only slightly increased in the primary TH because of minor carbohydrate volatilization. AD substantially increased these ratios to 1.8, 2, and 2.4 depending on the SRTs used. The high tCOD/VS ratios in the effluent of AD operated with shorter SRTs indicates incomplete biodegradation, probably with more lipids residue because lipid digestion is the slowest among the three components, and lipid biodegradability cannot be enhanced by TH (Alhraishawi and Aslan, 2022; Barber, 2016). After AD, all tCOD/VS ratios monotonously decreased to 0.9 with more treatments probably due to the depletion of lipids and proteins. The remainder might be the recalcitrant carbohydrates such as cellulosic biomass.

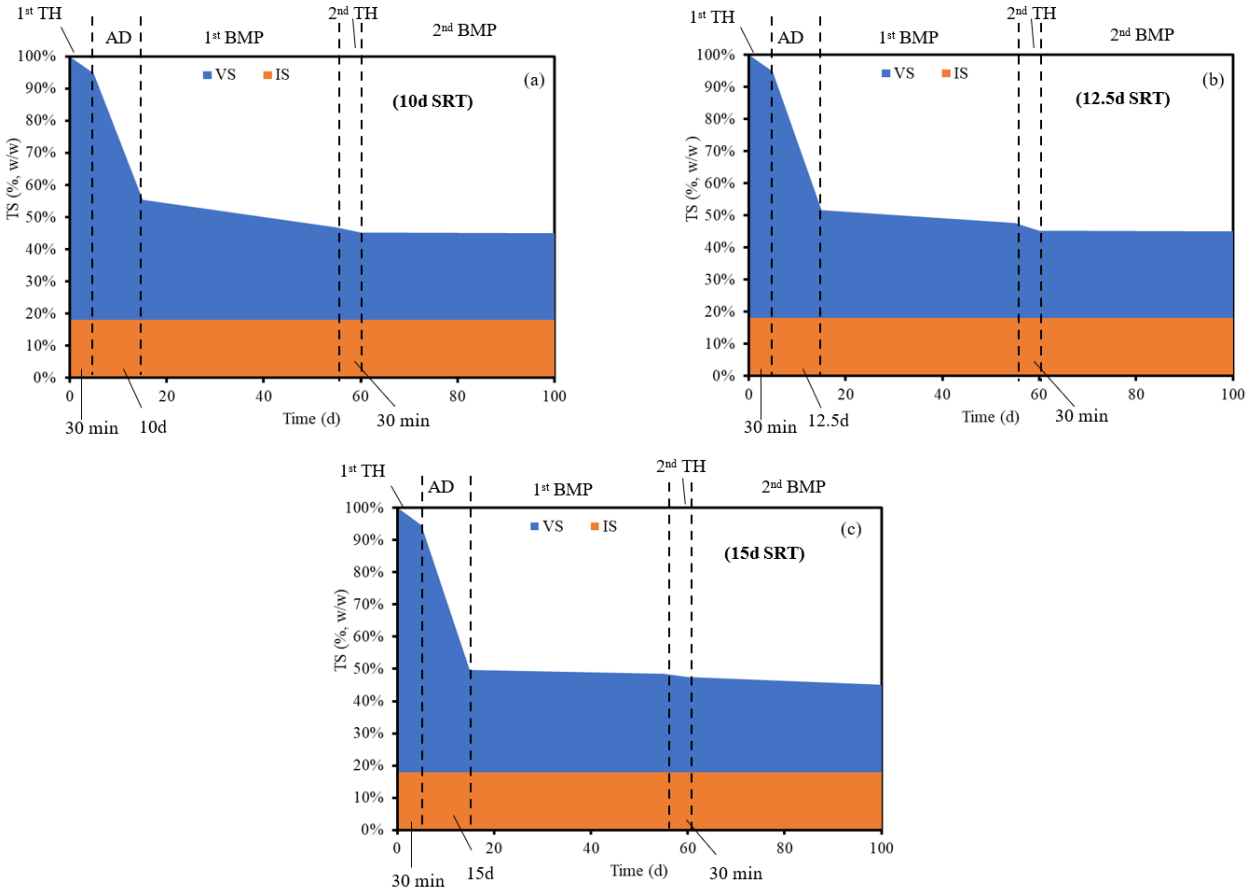

Figure 6.7. TS, VS, and IS turnover in digestates produced from SRTs of (a) 10 days, (b) 12.5 days, and (c) 15 days throughout the TH-AD-BMP-TH-BMP treatments.

6.6 Discussion

6.6.1 Does a secondary TH increase sludge digestibility?

Although it has been previously reported that TH can enhance methane yield from AD for 8% - 20% due to the capacity of TH in hydrolyzing particulate organics that cannot be biologically hydrolyzed in AD (Ferrentino et al., 2019; Gonzalez et al., 2018; Vavouraki et al., 2013; Yeshanew et al., 2016), this study is the first to report that a secondary TH actually created new BMP from sludge whose biodegradability had been exhausted in a prior BMP test (Figure 6.3b). About 15-20% extra methane was produced from the newly formed sCOD in the secondary TH (Figure 6.2b).

In our opinion, there are at least three contributors to the new sCOD created during the secondary TH. First, it is known that alkaline TH is more effective than acidic TH when it comes to the hydrolysis efficiency (Takashima, 2008; Yang et al., 2019b). Therefore, a portion of the recalcitrant organics that was not hydrolyzed in the primary TH is reasonably broken down into sCOD in this secondary TH as a result of the dramatic pH difference between the two TH (Figure 6.5a). Second, the sCOD produced during the second TH was not only from the degradation of recalcitrant organics but also from the new cells grown during AD and primary BMP. Assuming the biomass yield during the anaerobic digestion of municipal sludge was $Y_{\Delta cell/\Delta COD}$ = 0.06 g cell COD g^{-1} substrate COD (Batstone et al., 2002), sCOD contribution from new cell hydrolysis in the secondary TH could maximally account for 40-50% of the total sCOD created. Third, according to Figure 6.8, the function of TH is hydrolyzing pCOD into sCOD, and this function is known to be played though the TH temperature and time (Kakar et al., 2022). As literature reviewed in Figure 6.8, sCOD yield from TH calculated as ΔsCOD/pCOD tended to monotonously increase with the TH time in all five studies investigating the TH time effect on municipal sludge hydrolysis. It is interesting to observe that 30 to 40 min of TH duration appeared to be the optimal condition that offered the greatest sCOD yield within the shortest TH duration, beyond which the sCOD yield still increased but tended to reach plateau after 60 min (Ferrentino et al., 2019; Lu et al., 2014; Wu et al., 2021; Xue et al., 2015; Zhang et al., 2017). One possible explanation is that majority of the organics in the sludge such as EPSs and cells walls can be easily hydrolyzed in TH within 30 min and thus contributed to the largest fraction of sCOD yield for methane production (Barber, 2016). However, some recalcitrant fraction of organics in the sludge such as cellulosic biomass may need a much longer time to be hydrolyzed (Luo et al., 2022; Zhang et al., 2015). Similarly in this study, TH-AD harvested about 0.49-0.55 L CH_4 from each gram VS fed into the system (Figure 6.3b), indicating that a 30 min TH at 165 ˚C followed by the 10-15 days of SRTs of ADs was sufficient to recover majority of sludge BMP. Although there was only 0.09-0.11 L CH_4 g^{-1} VS_{fed} BMP left in the TH-AD digestates, another 30 min secondary TH was able to create another 0.09-0.12 L CH_4 g^{-1} VS_{fed} new BMP from the recalcitrant fraction of the BMP sludge (Figure 6.2b). This new BMP accounted for about 13-17% total BMP of the raw sludge measured in Figure 6.2b, which appears to be in line with the sCOD yield in TH after 30 min in Figure 6.8. Similar observation was reported by (Takashima, 2008) when TH time was increased from 30 to 60 min. Therefore, a techno-economic assessment is definitely needed to evaluate the benefit of a secondary TH.

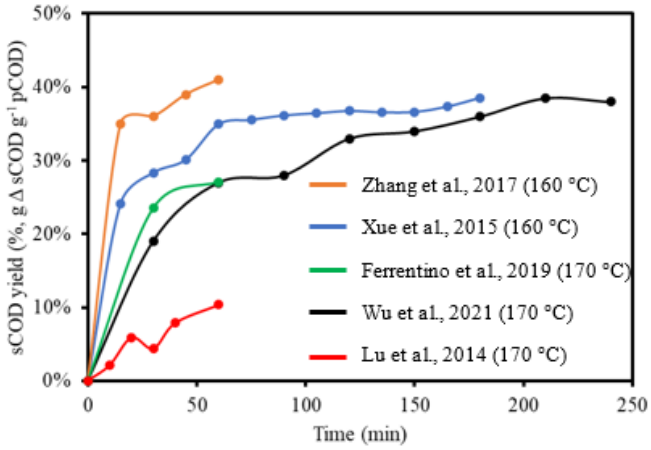

Figure 6.8. Effect of thermal treatment time on municipal sludge sCOD yield from previous published works (Ferrentino et al., 2019; Lu et al., 2014; Wu et al., 2021; Xue et al., 2015; Zhang et al., 2017). The TH temperature used is indicated in the brackets.

6.6.2 Is the high level of sCOD in TH-AD effluent biodegradable?

The fact that adding a TH pretreatment to AD tends to produce digestate containing a significantly higher level of sCOD (e.g., 6900 to 7150 mg L^{-1}) was confirmed in this study (Figure 6.2a). The two rounds of BMP tests in this study have proven that this sCOD in TH-AD digestate is non-readily biodegradable under anaerobic condition, and even a secondary TH treatment still cannot improve its biodegradability. A previous rDON study using the cake from the same WRRF has produced a similar level of sCOD out of TH-AD, e.g., 6000 mg L^{-1} (Zhang et al., 2021a). Non-biodegradable substances such as melanoidins produced from the Maillard reaction occurring between amino acids and reducing sugars in TH has been regarded as the cause of this recalcitrant sCOD formation (Zhang et al., 2021a), which explains why the sCOD was recalcitrant to the two rounds of BMP test and even a secondary TH did not help.

6.7 Conclusions

The following concluding remarks can be drawn from this study:

1. A secondary TH was able to create new BMP by converting 18-22% recalcitrant pCOD to sCOD, which accounts for 17-25 % methane yield in AD.
2. A secondary TH did not appear to be able to improve the digestibility of recalcitrant sCOD or rDON.
3. A secondary TH can increase the sludge pH to a peak value of 9.2, which is opposite to a primary TH in which pH was at the lowest point of 5.7.
4. A secondary TH did not contribute to VSR. The majority of VSR was achieved in AD especially when a 15-day SRT was used.

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Chapter 7 Aeration in sludge holding tanks as an economical means for biosolids odor control—A case study

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7.1 Abstract

Abnormally high odor detection threshold (DT) values were detected for biosolids produced at one of the Washington Suburban Sanitary Commission's (WSSC Water) Water Resource Recovery Facilities (WRRFs), affecting the subsequent landfill disposal. Therefore, immediate identification of the source and cause of the excessive biosolids odor was needed. At the same time, as an inexpensive countermeasure, aeration of thickened sludge holding tanks (SHTs) was tested as a solution for mitigating the subsequent biosolids odor emission. Experimental results indicated that the extremely low oxidation reduction potential (ORP) in the SHTs and the fermentation of high-rate activated sludge and not the nitrification or denitrification activated sludge that primarily contributed to the odor emission from the dewatered cake. Two rounds of bench-scale experiments on different days confirmed that aerating the sludge in holding tanks reduced peak emission concentrations of sulfurous odorous compounds such as hydrogen sulfide (H_2S), methanethiol (MT), and dimethyl sulfide (DMS) from 203, 110, and 20 mg m^{-3} g^{-1} dry to 119, 70, and 14 mg m^{-3} g^{-1} dry, respectively. Further preliminary full-scale validation showed that even a slight ORP improvement from -180 mV to -162 mV reduced the peak H_2S concentration from 87 to 48 mg m^{-3} g^{-1} dry and decreased the biosolids DT value from 4266 to 1862. It was concluded that lifting ORP in SHTs through aeration can be used by utilities as a simple means for biosolids odor control.

7.2 Keywords

Anaerobic; ORP; H_2S; MT; DMS; Odor Detection threshold

7.3 Graphical abstract

7.4 Introduction

A Water Resource Recovery Facility (WRRF) administrated by the Washington Suburban Sanitary Commission (WSSC Water) has been facing the pressing challenge of excessive biosolids odor. The biosolids from this WRRF, which has an average capacity of ~30 million gallons per day, are not currently permitted as Class B biosolids, limiting their disposal options to landfilling. Over the past several years, landfills have expressed reluctance to accept biosolids from this WRRF and rejected loads in certain instances. WSSC Water is therefore actively looking for cost-effective strategies to reduce biosolids odor and decrease the risk of further increasing costs associated with solids hauling and disposal. Beginning in 2024, dewatered cake from this and other WSSC Water WRRFs will be hauled to WSSC Water's centralized bioenergy facility to be further treated through thermal hydrolysis and anaerobic digestion. Because of this, WSSC Water elected to focus on solutions that require relatively low capital investment.

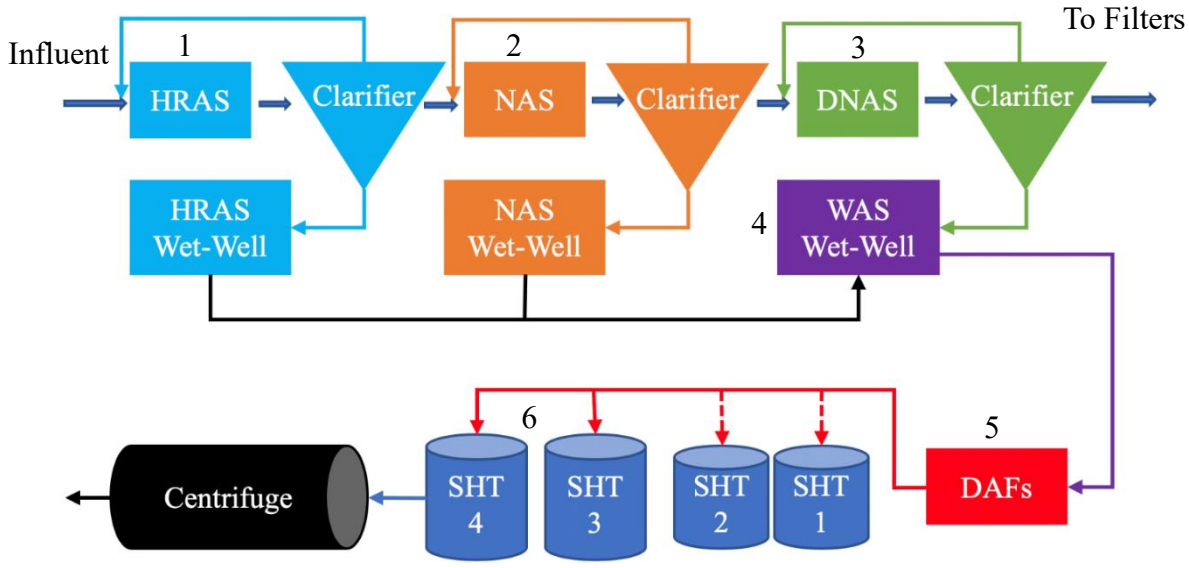
As illustrated in Figure 7.1, this WRRF has a three-sludge biological process: (1) high-rate activated sludge [HRAS], (2) nitrification activated sludge [NAS], and (3) denitrification activated sludge [DNAS]. Waste sludge streams from these three processes are combined and then thickened using dissolved air flotation (DAF). Following the DAF, thickened sludge is stored in sludge holding tanks (SHTs) before being dewatered with centrifuges which are operated 24 hrs day^{-1} and 5 days $week^{-1}$. Because the dewatering system is offline during weekends, thickened sludge from

the DAFs is temporarily stored in SHTs 3 and 4 (Figure 7.1) until dewatering resumes on Monday morning. Circulation pumps are used to keep the sludge suspended in SHTs 3 and 4.

The dewatered biosolids produced from the centrifuge exhibits exceptionally high odor emission. Typical odor-causing compounds emitted from biosolids include hydrogen sulfide (H_2S) and volatile organic sulfur compounds (VOSCs) such as methanethiol (MT) and dimethyl sulfide (DMS) (Novak et al., 2006). It is widely accepted that these odorous compounds are mainly generated from anaerobically fermented organic materials (Higgins et al., 2006; Schlegelmilch et al., 2005). More specifically, H_2S and MT are the microbial degradation by-products of sulfur containing amino acids such as methionine and cysteine (Higgins et al., 2006), which have been shown to be present in protein extracted from activated sludge and anaerobically digested sludge (Dignac et al., 1998; Higgins et al., 2004; Morgan et al., 1991). Moreover, MT and DMS have also been found to be the products of methylation of H_2S and MT by anaerobic bacteria (Bak et al., 1992; Lomans et al., 1997). It should be noted that in the presence of sulfate, sulfite or thiosulfate, sulfate reducing bacteria (SRB) are also able to convert these substrates to H_2S under anaerobic condition (McCarty and Smith, 1986).

Although there are various existing physical, chemical, and biological methods available for sulfurous odor control such as dry or wet adsorption, membrane separation, chemical precipitation, or even the replacement of high shear centrifuge with low shear belt press (Erdal et al., 2008), these conventional approaches require significant capital, material and/or chemical investment. In contrast, dosing air to improve the oxidation reduction potential (ORP) within the SHTs holds promise to provide a simple and economical solution for biosolid odor control. This is because previous studies have indicated that aeration can not only reduce the average hydrogen sulfide concentration in biogas of the anaerobic digesters (Krayzelova et al., 2014) but also reduce the odor emission from anaerobically digested biosolids (Winter et al., 2004). Although very little is known about the effect of SHT aeration on odor control of the biosolids produced from this WRRF without anaerobic digestion, it can be hypothesized that very similar mechanism can be expected in the anaerobic environment of the SHTs. Therefore, the objectives of this study were to verify this hypothesis and then develop a simple and cost-effective means for biosolids odor control. It

is our anticipation that the outcome from this case study will provide engineering guidance for wastewater utilities with budget constraints and similar odor control needs.



Information:

1) SHTs 1 and 2 are spare tanks equipped with pump circulation and aeration apparatus;

2) SHTs 3 and 4 are routinely used tanks equipped with pump circulation but without aeration apparatus

Figure 7.1 Flow chart of the sludge handling system at the studied WRRF

7.5 Material and methods

7.5.1 ORP profiles measurement

Two handheld ORP meters (MTC 101 probe, Hach, Loveland, Colorado) were used to measure replicate ORP values throughout this WRRF's solids handling stream as shown in Figure 7.1. More specifically, two 3 L sludge samples were collected from locations 1 to 6 in Figure 7.1. Two ORP probes were inserted into the samples separately and allowed to stabilize for 5 minutes before

reading. To increase the confidence of ORP profiles measured in this study, two separate ORP profiles were measured in two different field events on 25 days apart.

7.5.2 Sludge combination study

Fresh HRAS, NAS, and DNAS sludges with total solids (TS) of ~0.5 % (g g^{-1}) were collected from the WRRF and blended at bench scale according to the actual blending ratios used in the full-scale WRRF. To infer the contribution of individual or combinations of sludges on the odor emission from dewatered cake, all seven possible combinations of the three types of sludge were tested (Table 7.1). The seven groups of blended sludge were then thickened using a lab centrifuge (Sorvall Legend X1R; Fisher Scientific, Waltham, MA) under a centrifugal acceleration of 2940 g for 2 min to achieve TS of ~4% which is similar to the value after the DAFs at the full scale. Finally, the thickened sludge was placed in 300 ml enclosed bottles for 64 hours to mimic sludge storage in the SHTs and then dewatered to approximately 20% TS using the lab-scale dewatering apparatus described below and used in a previous study (Zhang et al., 2020). TS and volatile solids (VS) contents of seven groups of dewatered biosolids were provided in table 7.1. The seven groups of dewatered biosolids were then placed in 300 ml glass jars to perform odor emission analysis.

Table 7.1. Seven combinations of the three types of thickened sludges

Group	HRAS:NAS:DNAS (V:V:V)	Dewatered cake TS (g g^{-1})	Dewatered cake VS (g g^{-1} TS)
HRAS	1:0:0	18%	82%
NAS	0:1:0	19%	77%
DNAS	0:0:1	20%	68%
HRAS+NAS	95:4:0	19%	83%
HRAS+DNAS	95:0:1	16%	82%
NAS+DNAS	0:4:1	20%	70%
3 in one	95:4:1	16%	82%

7.5.3 Bench-scale SHT aeration

Thickened sludge with TS of ~4% was collected from the end of the DAF system in Figure 7.1 and then divided into three groups: (1) Control: raw sample with neither mechanical mixed nor aeration; (2) Mechanical mixed without aeration; and (3) Mechanical mixed with aeration. Sludge samples with volume of 1 L were added into 1.5 L glass bottles. Mechanical mixing was provided with a magnetic stirring bar rotating at 150 rpm in order to mimic the pump circulation system in the full-scale SHTs. Aeration was provided by an air stone suspended in the middle height of the sludge bed with an air flow rate set at 2.7 L min^{-1}. All bottles were sealed with parafilm. A 1 cm diameter hole was punched on the parafilm to simulate the inadequate airtightness status of full-scale SHTs. All sludge groups were prepared in duplicate and held for 64 hours with pH and ORP measured daily. After 64-hour holding time, all groups were dewatered and then placed in glass jars for odor emission analysis.

7.5.4 Full-scale SHT aeration

Effect of aeration in the SHT on odor emissions from dewatered cake was also confirmed in a full-scale test. The studied WRRF has four SHTs, numbered SHTs 1, 2, 3, and 4 (Figure 7.1). Normally, only SHTs 3 and 4, which are larger in size and do not have aeration equipment, are used to hold thickened sludge prior to dewatering. In contrast, SHTs 1 and 2 (Volume ~1.2 x 10^5 L in each) are equipped with aeration diffuser grids and used for backup. In this study, continuous aeration at an air flow rate of 3540 L min^{-1} was provided to SHTs 1 and 2 using diffuser grids across the entire bottom of these two tanks for 65 hours over the weekend until the start of the dewatering process on Monday. ORP values were measured for both aerated and non-aerated sludge after 65 hours of holding in the full-scale SHTs. The sludge samples were then dewatered at full scale and divided into three groups depending on the aeration and autoclave treatment applied, i.e., (1) mechanically mixed only; (2) mechanically mixed + aeration; and (3) mechanically mixed + aeration + autoclave. All the groups were prepared in duplicate. The sludge samples were autoclaved in capped jars at 120 ºC for 15 min. The purpose of autoclaving the sludge samples was to eliminate all biological activity to determine whether the odor was controlled through biological activity inhibition or

physical air stripping during the SHT aeration. Finally, the odor emission analysis was conducted for all three groups of sludges.

7.5.5 Dewatering at bench scale

A bench-scale dewatering system was established to mimic the mechanism of dewatering processes in full-scale application. Sludge samples (300 ml) were mixed with 80 ml polymer with 60% cationicity and 41% active polyacrylamide (Clarifloc, C-6226, Polydyne Inc, Riceboro, GA) and then sheared in a commercial blender (Waring MX1200XTXP; Stamford, CT) under controlled shear intensity quantified by $G \bullet t$ at 10^5 in which G is the mean velocity gradient and t is the time taken for sludge to be exposed to shear force. This shear intensity was calculated based on the information of the full-scale centrifuge used at the WRRF. The mixture was then preliminarily dewatered using a lab centrifuge at 5762 g for 15 min, followed by further mechanical compression to produce dewatered cake using a piston press under controlled pressure of 413 kPa and for 30 min. More detailed information about the dewatering apparatus can be found in our previous study (Zhang et al., 2020).

7.5.6 Odor emission analysis

Serum jars that were 300 ml in volume were loaded with ~20 g dewatered cake samples and then purged with nitrogen gas to remove headspace oxygen. The jars were sealed with rubber stoppers and incubated at the room temperature. Simultaneously, a 1 L air bag (Tedlar, Complex Plastics, Indiana UAS) was connected to normalize the air pressure inside of each jar. The concentrations of odorous compounds (H_2S, MT, and DMS) in the headspace of jars were monitored on a daily basis to obtain the odor emission profiles along with the sludge storage time.

7.5.7 Olfactometry analysis

Biosolid samples were sent to the Penn State University Olfactometry Lab to quantify the odor Detection Threshold (DT) using methods described elsewhere (Quality, 2003; St. Croix Sensory, 2003). The DT represents the lowest odor concentration that can be sensed by a panel of odor assessors as being different from odor-free air. For example, an odor DT of 1,000 indicates that an odor can be sensed if diluted with odor free air at a ratio of 1/1,000. This is the metric mostly often used to define the odor concentration in environmental odor studies (WRF, 2019).

7.5.8 Chemical analysis

The contents of odor compounds such as H_2S, MT, and DMS in the headspace of jars were measured using a gas chromatograph (GC) equipped with a flame ionization detector (GC-2014, Shimadzu, Columbia, MD) and a 60 m long capillary column with 0.53 mm diameter (Agilent, DB-1, Santa Clara, California). Headspace gas volume of 40 ml was collected using a 50 ml gas-tight syringe (Hamilton, Reno, Nevada) on a daily basis and manually injected into the GC. Standard gases (Airgas, Inc., Radnor, Pennsylvania) were used to develop the calibration curves for these odorous compounds.

7.5.9 Statistical analysis

The values of ORP, pH, and concentrations of H_2S, MT, and DMS are presented as the sample mean with standard errors shown in the error bars.

7.6 Results

7.6.1 Abnormally high odor emission from WRRF biosolids

According to the biosolids odor assessment results shown in Figure 7.2, the odor DT of lime-amended biosolids from the studied WRRF was reported as 2512, which was almost three times as odorous as lime-stabilized biosolids from WSSC Water's another WRRF (DT = 864) (Figure 7.2). The biosolids odor DT from the studied WRRF was also compared to previously published biosolids odor DT values by Water Research Foundation (WRF, 2019). In that report, biosolids samples taken from 16 WRRFs were reported to have odor DTs ranging from 126 to 3236 with a mean DT approximately 1133 (Figure 7.2). Only one of the 16 samples had an odor DT value greater than that of the biosolids from the WRRF investigated in this study (Figure 7.2). Based on this comparison, it is clear that the biosolids from this studied WRRF exhibited an abnormally high odor DT value.

7.6.2 ORP profiles

Replicate ORP profiles in Figure 7.3 were measured at the studied WRRF during two separate field sampling events and showed very similar trends. The ORP dropped from 110 mV, 150 mV, and 120 mV in the HRAS, NAS and DNAS, respectively, to approximately -100 mV in the waste activated sludge (WAS) wet well once they were blended. Although the ORP remained unchanged in the DAF effluent (approximately -90 mV), it drastically dropped again to approximately -170 mV in the SHTs, which created ideal anaerobic conditions for the formation of odorous compounds such as H_2S, MT, and DMS. During the sampling events, the odor seemed to be greatest around the SHTs.

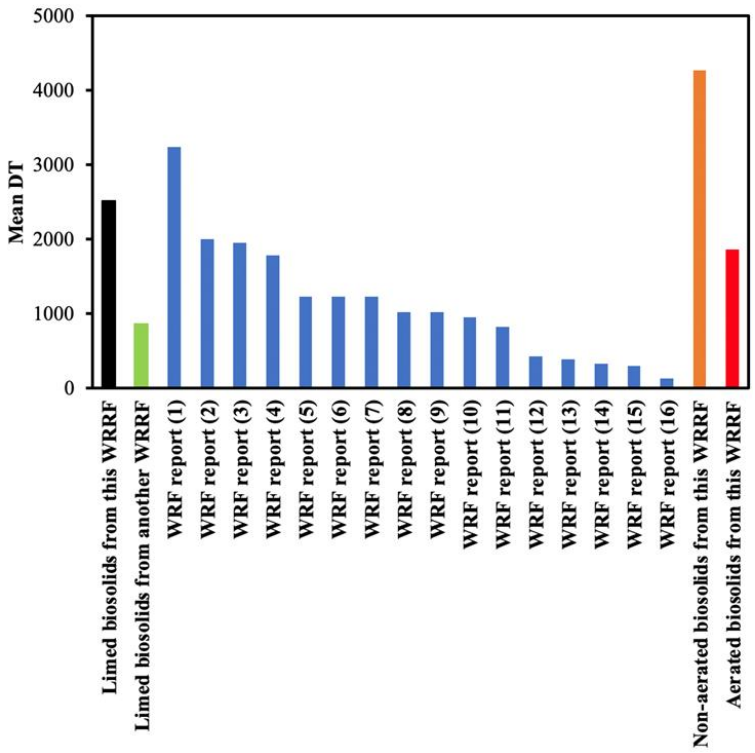


Figure 7.2. A comparison of limed biosolids DT values from this WRRF under current investigation and another WRRF administrated by WSSC Water, as well as the DT values of biosolids collected from 16 WRRFs as reported in WRF 2019 report. The biosolids DT values from this studied WRRF full-scale trial with and without SHT aeration are also shown.

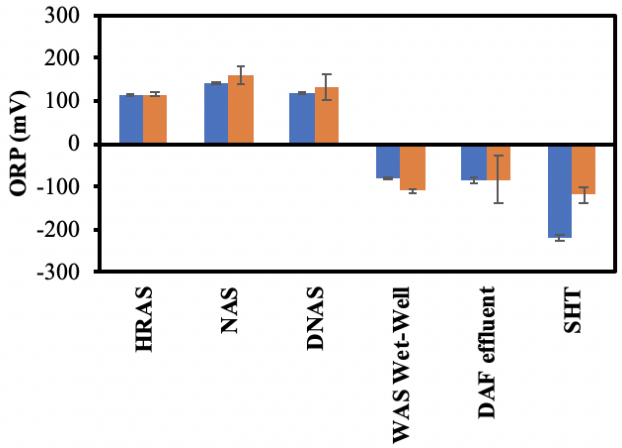


Figure 7.3. ORP profiles measured in two separate field trips sampling events at the studied WRRF

7.6.3 Source of the odor formation

As shown in Figure 7.4, a matrix of seven sludge combinations were tested to evaluate the contribution of HRAS, NAS, and DNAS to odor emission from dewatered cake (Table 7.1). Whenever HRAS was blended in, substantial levels of H_2S, MT, and DMS were generated from the dewatered cake. This can be possibly explained by the high protein fraction typically contained in the HRAS. A similar observation was reported previously (Hentz et al., 2000), which found that storing primary and waste activated sludges in separate sludge holding tanks can achieve 50-70% less odor from dewatered biosolids than storing both sludges together. In comparison, only negligible levels of H_2S, MT, and DMS were formed in NAS, DNAS, and NAS + DNAS. Hence, NAS and DNAS appeared to have very little to do with the source of odor emission.

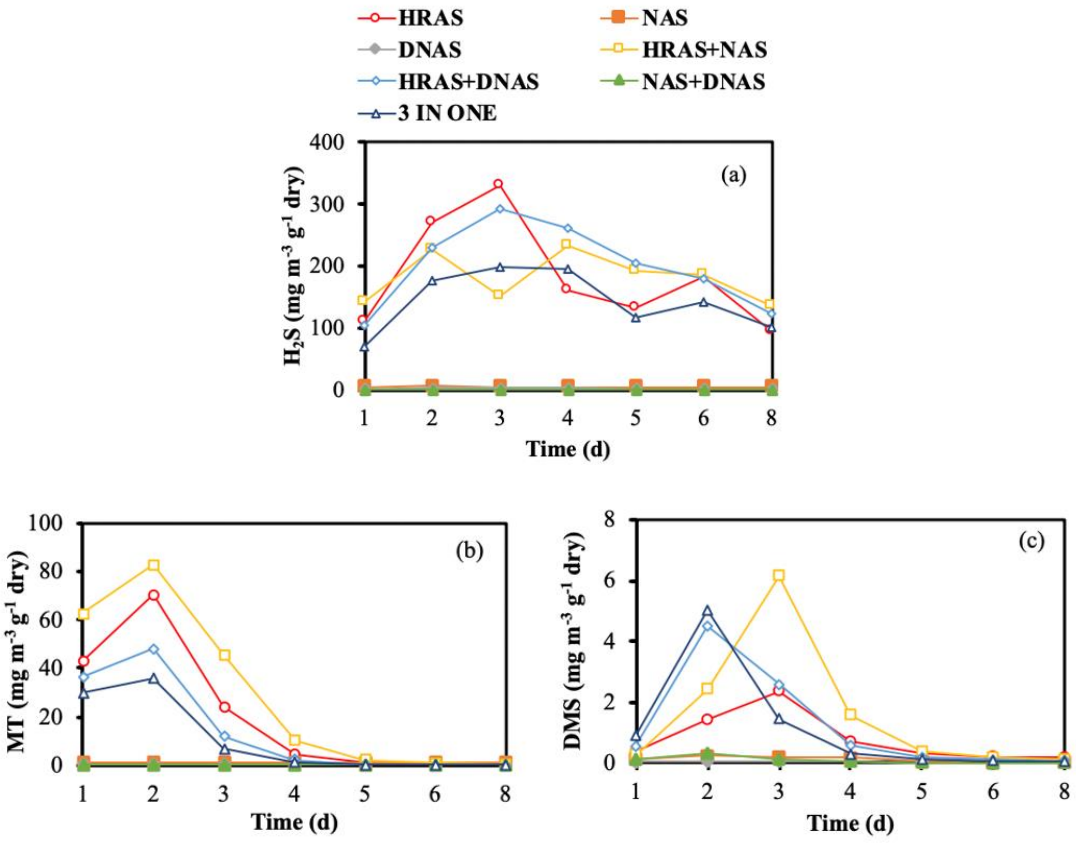


Figure 7.4. Profiles of (a) H_2S, (b) MT, and (c) DMS emission from dewatered cake during over time for the seven combinations described in Table 7.1.

7.6.4 Effect of lab-scale SHT aeration

Aeration of thickened solids during the 64-hour holding time was tested at bench scale as a potential odor mitigation strategy. As shown in Figure 7.5a, ORP in the aeration group increased gradually from -179 mV to -120 mV with continuous aeration over the simulated 64-hour storage time (i.e., became less anaerobic). The peak ORP was as high as -103 mV, which is approaching anoxic. In contrast, ORP values in the control group and mechanical mixed groups without aeration remained anaerobic at levels below -159 mV throughout the experiment. This indicates the inability of mechanical mixing, mimicking the pump circulation in full scale, to entrain enough air to increase the sludge ORP. Meanwhile, pH of the aeration group increased from 6.83 to 7.06 at the end of the holding time (Figure 7.5b). However, the pH in the other groups dropped from 6.83 to 5.98 and 6.35, respectively (Figure 7.5b). The plausible explanation is that anaerobic fermentation occurring in the mechanically mixed and control groups might have produced acids while the oxidization of organics in the aeration group produced alkalinity.

The three groups of sludges were dewatered after the 64-hour holding time, and the dewatered cakes were stored in glass jars to perform the odor emission analysis. The odor compounds were monitored until the concentrations reached low levels and/or stabilized, which is beyond the typical 1- to 3-day dewatered cake storage time. The dewatered cake from the aerated group exhibited the lowest peak levels of H_2S, MT, and DMS throughout the 17-day monitoring period compared to the mechanical mixed group and the control group (Figure 7.6 a and b). The most striking result was that the DMS emission peak for the cake that was aerated appeared the latest on day 8 and had the lowest peak DMS concentration (13.86 mg m^{-3} g^{-1}), which was approximately 30% lower than those of the other two groups (Figure 7.6c). This bench-scale experiment demonstrated that aeration during the thickened sludge holding time can reduce sulfurous odor emission from the dewatered cake.

To increase confidence in the results obtained from this first round of the bench-scale SHT aeration experiment prior to proceeding with a full-scale test, a second round of the bench-scale aeration testing was performed. The pH and ORP profiles from the second round of testing are shown in

Figure 7.7. The ORP measured in the aeration groups increased gradually from -170 mV to -120 mV as a result of continuous aeration over the 64-hour sludge holding time (Figure 7.7a), which was similar to the first-round experiment as shown in Figure 7.5a. The ORP in the control and mechanical mixed groups without aeration remained at a low level throughout the holding time, as well . Meanwhile, pH in these three groups also showed a similar trend as that in the first-round of testing as shown in Figure 7.5b, i.e., the pH of the aeration group increased from 7.37 to 7.55 at the end of the sludge holding time while the pH in the other groups dropped from 7.37 to 7.12 and 7.05, respectively (Figure 7.7b).

The same dewatering and odor analysis procedures that were used in the first round were repeated for the second round of testing. The aerated sludge cake still had the lowest concentrations of odorous compounds in terms of H_2S, MT, and DMS throughout the 23-day monitoring period compared to the mechanical mixed and the control groups without aeration during the same duration (Figure 7.8). Similarly, the cake from the control group had the highest H_2S, MT, and DMS peak levels, followed by the cake from the mechanically mixed group (Figure 7.8). Based on similar data obtained from two rounds of tests, it can be concluded with confidence that aeration during the sludge holding time is capable of reducing odorous compounds generated from the dewatered cake.

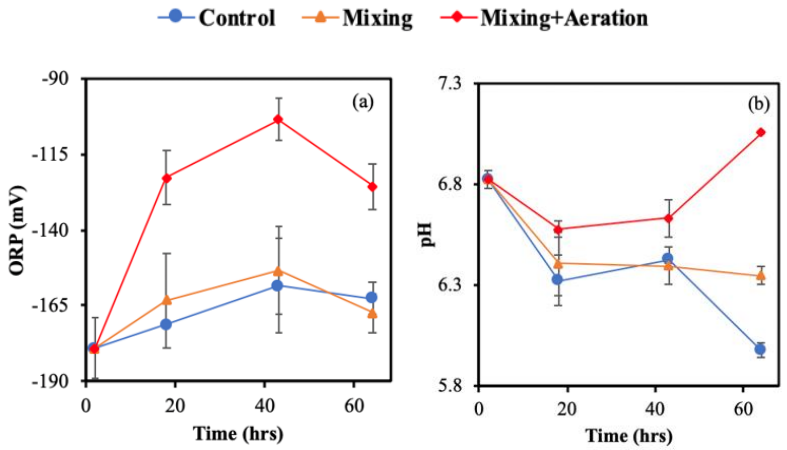


Figure 7.5. Profiles of (a) ORP and (b) pH measured during the 64-hour holding time in the first-round of bench-scale experiment mimicking the SHT environment.

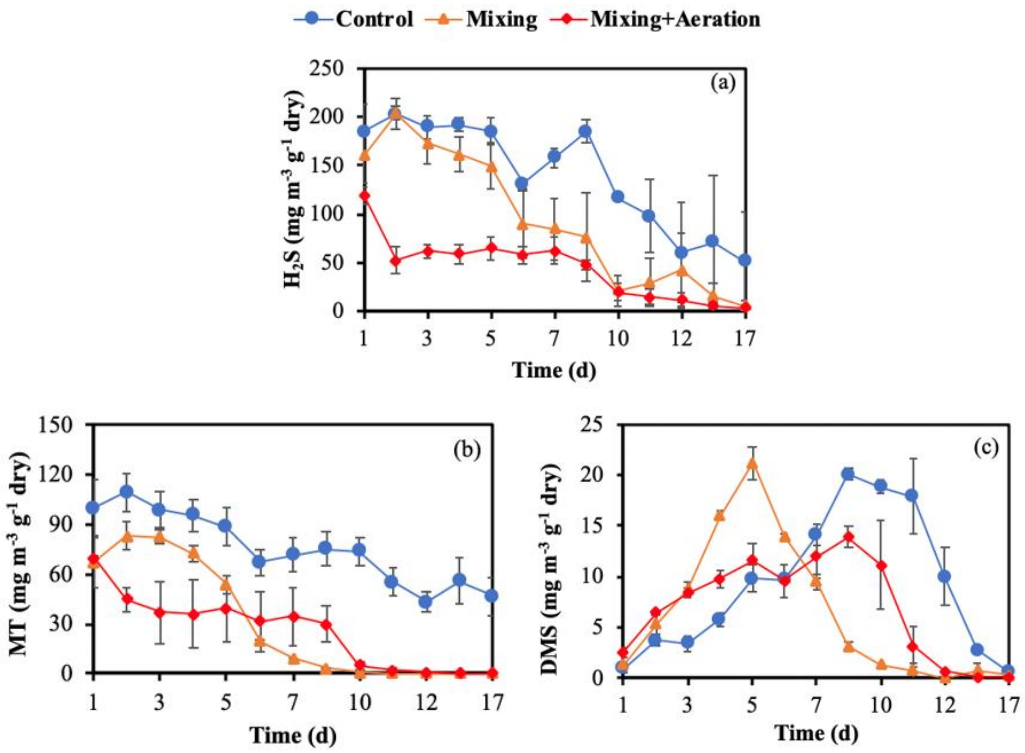


Figure 7.6. Profiles of (a) H_2S, (b) MT, and (c) DMS measured from dewatered cake over time after the three groups of thickened sludge were subjected to mechanical mixing and/or aeration at bench-scale. Results shown are for the first-round of bench-scale testing and were consistent with the second round.

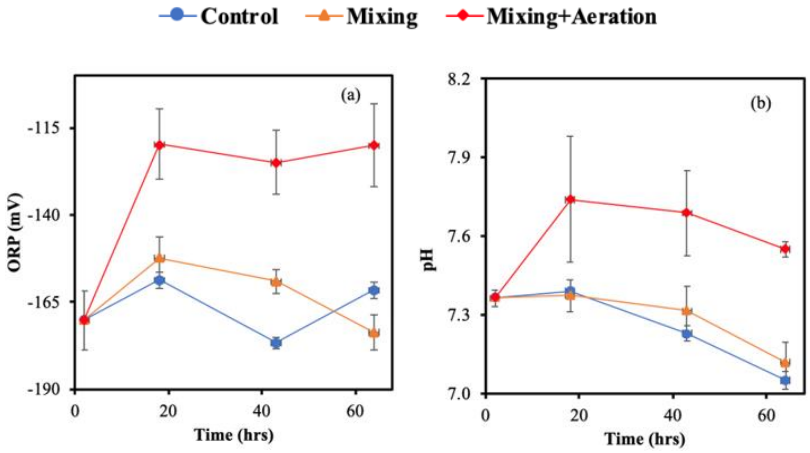


Figure 7.7. Profiles of (a) ORP and (b) pH measured in the course of the 64-hour sludge holding time in the second-round of bench-scale experiment mimicking SHTs.

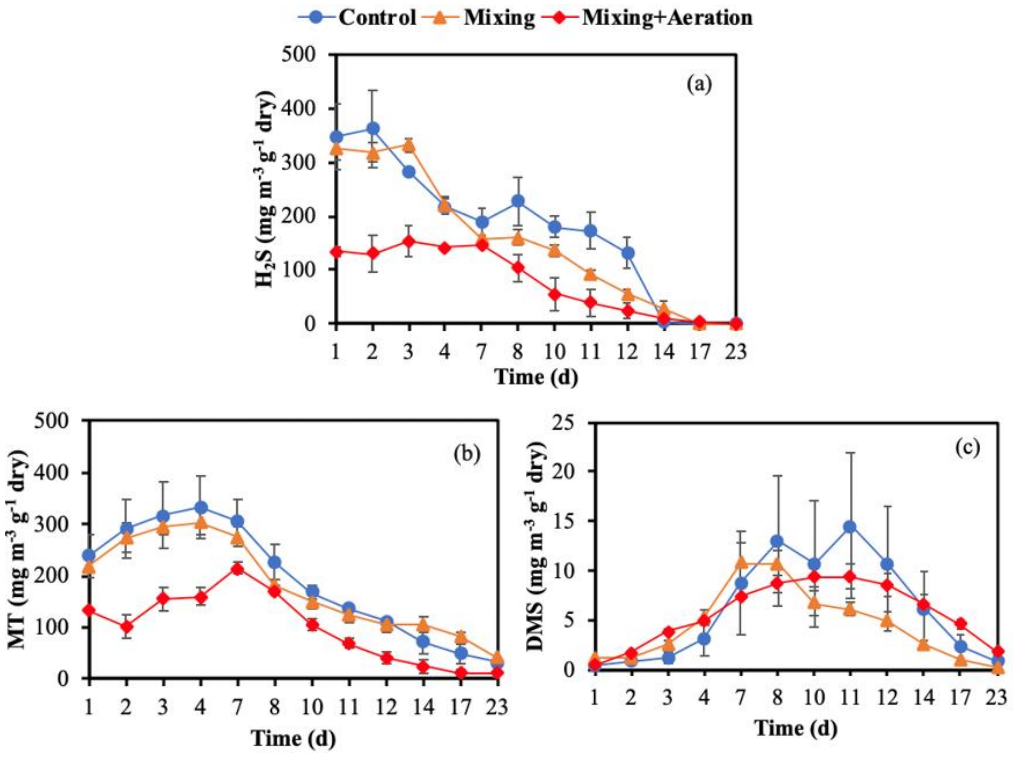


Figure 7.8. Profiles of (a) H_2S, (b) MT, and (c) DMS measured in the course of the sludge storage time for three groups of sludge with/without mechanical mixing and aeration in the second-round of bench-scale experiment mimicking SHTs

7.6.5 Preliminary full-scale trial of the SHT aeration strategy

After confirming favorable results in the two bench-scale SHT aeration tests, full-scale testing of aeration in SHTs 1 and 2 as an odor mitigation strategy was conducted. ORP was measured in the SHTs for both the aerated (SHTs 1 and 2) and non-aerated (SHTs 3 and 4) thickened sludges after 64 hours of holding time. The ORP value was -162 mV in the aerated sludge after ~64 hours of aeration, which was only about 18 mV higher than the ORP of the non-aerated sludge (-180mV; data not shown). This ORP improvement in the full-scale aerated sludge was not as high as that in the bench-scale experiments (Figure 7.5a). It is suspected that the aeration time for the samples collected at full-scale was below the targeted 64 hours due to the tank filling schedule for the solids operation during that timeframe. Additional full-scale testing is planned.

Dewatered cake samples with or without aeration pretreatment in the full-scale holding tanks were collected after full-scale centrifugal dewatering but before lime addition. The odor emission profiles were obtained for three groups of dewatered samples. Consistent with bench-scale results, the full-scale aerated sludge cake had the lowest concentrations of H_2S emission throughout the 14-day monitoring period compared to the mechanical mixed cake during the same duration through pump circulation (Figure 7.9 a and b). However, there was not much difference between the two groups in terms of MT concentration (Figure 7.9b). Moreover, only minor levels of DMS were produced (Figure 7.9c), indicating that the major odorous compounds emitted from the full-scale dewatered cake were H_2S and MT. In view of this experimental result inconsistency which probably can be attributed to the insufficient aeration, the DT values of dewatered cakes with and without aeration were measured and shown in Figure 7.2. As can be seen, the aerated sludge cake (DT = 1862) was approximately 56% less odorous than the non-aerated sludge cake (DT = 4266) (Figure 7.2), suggesting that aeration in the full-scale SHTs indeed mitigated the odor emission from dewatered biosolids.

It was also of interest to identify the mechanism causing the reduction in odor emission from the dewatered cake. It is our hypothesis that the aeration in the SHTs can inhibit the activity of odor-producing microorganisms during the holding time, and further affect the odor emitted from the dewatered cake. However, a previous study also indicated that the aeration of wastewater can reduce the H_2S emission in the wet wells of lifting stations by stripping off dissolved H_2S to the air (Tomar et al., 1995). Therefore, another plausible explanation is that the aeration in the SHTs can strip off the dissolved odorous compounds to the air, leading to lower concentrations of dissolved odorous compounds in the dewatered cake going through the dewatering process and thus resulting in even less volatilization after dewatering. The autoclave process designed in this experiment was to verify whether the physical volatilization of the odorous compounds was a primary contributor to the odor reduction by eliminating the biological processes occurring in the dewatered cake. As shown in Figure 7.9, only negligible odorous compounds in terms of H_2S and MT were emitted from sludge cake autoclaved in capped jars. The sludge treated under the same conditions but without being autoclaved produced much higher H_2S and MT levels (Figure 7.9 a and b), proving that it is actually the change in biological but not the physical process that has reduced odor emission during the holding time in this study.

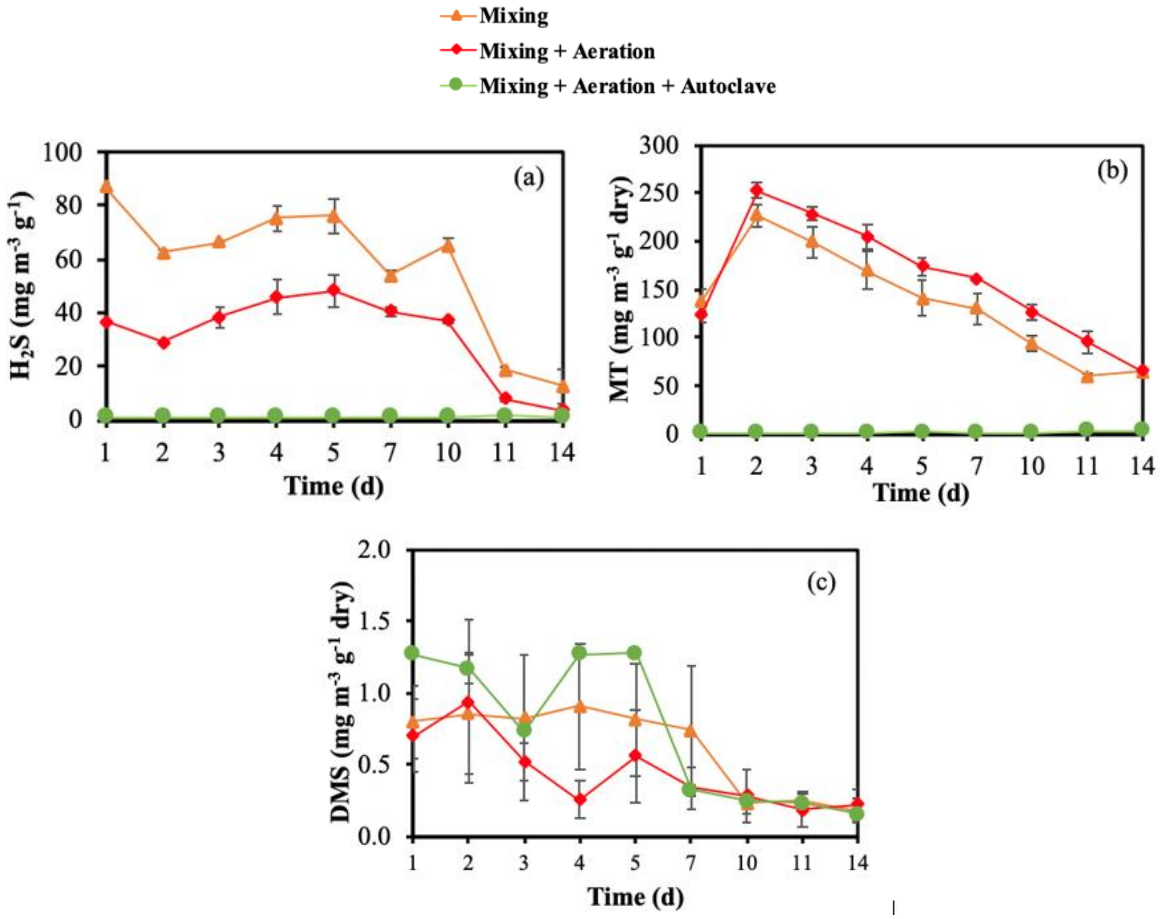


Figure 7.9. Profiles of (a) H_2S, (b) MT, and (c) DMS measured along with the sludge storage time for mixing only, mixing + aeration, and mixing + aeration + autoclave sludge samples taken from dewatering centrifuge in the full-scale study.

7.7 Discussion

Previous studies found that microaeration that increased the ORP above -100 mV can lead to the reduction of H_2S production as a result of the sulfate reduction activity inhibition (Ding et al., 2007). The average hydrogen sulfide removal in biogas of the anaerobic digesters can also be as high as 73% under microaeration condition in the anaerobic digester (Krayzelova et al., 2014). Likewise, previous work has also revealed that peak MT concentration under high rate aeration (0.3 L kg^{-1} dry min^{-1}) during kitchen waste composting was four times lower than that under low rate aeration (0.1 L kg^{-1} dry min^{-1}) (Zhang et al., 2016). As a matter of fact, the effect of aeration on odor control has also been studied in the other fields, such as livestock manure slurry storage.

For instance, 6.3 days of aerobic treatment of pig slurry achieved a reduction of the odor offensiveness rating from strongly offensive odor to faintly offensive odor (Burton et al., 1998). Although there are few published works related to the effect of SHT aeration in WRRFs, the results from this study revealed that even a slight increase of ORP from -180 mV to -162mV in SHTs achieved through aeration might have compromised the activity of odor producing bacteria in the dewatered cake.

The difference in terms of odorous compound emission from the sludge with and without being autoclaved suggests that it was the reduced anaerobic biological activity but not the air stripping during aeration that has primarily contributed to the reduction of odorous compound emission during the sludge holding time (Figure 7.9 a and b). Therefore, it is highly possible that the ORP increase as a result of the aeration might have inhibited the activity of odor producing bacteria in the dewatered sludge cake. Previous work indicated that the sulfate reduction predominated within the ORP range of -300mV to -400 mV, while the ORP range of -50 mV to -150 mV as was achieved in SHT aeration in Figure 7.5a was actually predominated by denitrification (Zhang et al., 2014). Likewise, the population of SRB was found to decrease by three to five orders of magnitude after two days of exposure to oxygen (Sass et al., 2002), and only a few species of SRB can escape oxygen toxicity (Krekeler et al., 1998). Thereby, it can be inferred that the aeration in the SHTs must have inhibited the activity of odor-producing bacteria and in turn controlled odor emission from later dewatered sludge cake.

7.8 Practical Implications

Both bench-scale and full-scale aeration experimental results in this study indicate that aeration in the SHTs during sludge holding time can effectively reduce the odor generation from the dewatered biosolids. Comparing to the other available odor control methods such as membrane separation and chemical precipitation, the only energy consumption of aeration is the air input, which is presumably economical and needs future evaluation. However, aeration in the SHTs may bring adverse effects on the sludge operation system. For example, previous study indicated that aeration can oxidize the sulfide in the sludge to the elemental sulfur, which may deposit on the walls and pipes and clog the SHTs (Krayzelova et al., 2015). Moreover, volatile compounds such as

ammonia and benzene can be stripped from the sludge during aeration (Kinidi et al., 2018; Phillips, 1995). The newly contaminated air released from SHTs by air stripping will need further treatment to avoid air pollution.

Full-scale test in this study showed limited reduction in odors, likely due to insufficient airflow and/or duration in the tested holding tanks. Therefore, in the next phase of study, additional full-scale testing will be completed for SHTs 1 and 2 to see if a more controlled or longer aeration duration in the sludge holding tanks is more effective in reducing odors. An engineering consulting firm is also being retained by WSSC Water to evaluate and develop costs for several solids aeration alternatives for SHT 3 and 4 including aeration with the existing blower system, a new blower, and Venturi aspiration of recycle pumps.

7.9 Conclusions

In the present work the cause, source, and the solution of the excessive biosolids odor issue in a WSSC Water's WRRF were summarized in Table 7.2. The following concluding remarks can be drawn from this study:

1) Abnormally high biosolids odor can be largely attributed to the storage of thickened sludge in the absence of oxygen for > 48 hrs.
2) HRAS but not NAS and DNAS turned out to be the major contributor to biosolids odor emission.
3) Lifting ORP levels in SHTs through aeration should be considered as a cost-effective measure for biosolids odor control.
4) The SHT aeration is thought to have inhibited the activity of odor producing bacteria and in turn reduced odor emission from dewatered biosolids.

Table 7.2. Summary of the cause, source, and solution of the excessive biosolids odor issue in a WSSC Water's WRRF

	Hypothesis	Experimental plans	Results
Cause of the biosolids odor	Anaerobic storage of waste sludge is the main cause of the biosolids odor	ORP profiles were measured throughout all treatment processes	Extremely low ORP in the SHTs creates the ideal condition for the formation of odorous compounds
Source of the biosolids odor	High fraction of HRAS in the combined waste sludge is the main cause of the biosolids odor	Seven groups of sludge samples were created with difference blending ratio in order to identify the major source of the biosolids odor	Only the groups with HRAS blended in exhibited substantial levels of odorous compounds, indicating that HRAS is the main source of the biosolids odor
Solution of the biosolids odor	Aeration in the SHTs during sludge holding time may reduce the odor emission from dewatered biosolids	Aeration was provided in both bench-scale and full-scale SHTs during sludge holding time	Bench-scale aeration test indicated that aeration could increase ORP and effectively reduce biosolids odor
			Full-scale validation was not as effective as in bench-scale, probably due to the insufficient aeration

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