Assessing the Role of Magnetite in Municipal Wastewater Treatment

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ASSESSING THE ROLE OF MAGNETITE IN MUNICIPAL WASTEWATER TREATMENT

by

Patricia Ayaa

A dissertation submitted in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

Civil and Environmental Engineering

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2022
ABSTRACT

Assessing the Role of Magnetite in Municipal Wastewater Treatment

by

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Utah State University, 2022

Major Professor: Dr. Michael McFarland
Department: Civil and Environmental Engineering

Some municipal wastewater treatment (MWWT) facilities are adopting the use of micrometer-sized magnetite particles through a technology called BioMag® to help them meet effluent nutrient (nitrogen and phosphorus) regulatory requirements. There is limited information, however, on the mechanisms and efficiency of these magnetite particles in nitrogen (N) and phosphorus (P) removal during the biological secondary wastewater treatment process. This research, therefore, estimated the effect of the magnetite on N and P removal in MWWT, with a case study of the Marlay-Taylor Water Reclamation Facility in Maryland. The intervention analysis model was used. However, a different approach to the forecasting methodology was proposed. Results showed significant improvement in N and P removal due to magnetite, improvements in treatment capacity, and in operating parameters like the sludge volume index and mixed liquor suspended solids. An account of the nutrient removal mechanisms by magnetite was also included.

Because some MWWT facilities use anaerobic digestion (AD) for sludge stabilization, this study conducted laboratory-scale AD experiments to investigate the
potential effect of magnetite-infused sludge from the MWWT process on biogas and hydrogen sulfide (H\textsubscript{2}S) gas production during AD, the extent of solubility of the magnetite, and its possible implications. Results showed no significant changes in methane yield as reported by some researchers who added magnetite to anaerobic digesters, although the hydrogen sulfide in the biogas decreased significantly. An increase in dissolved iron was also observed.

Finally, the possibility of elemental sulfur (S\textsuperscript{0}) formation during the AD process was investigated. A few studies that added Fe\textsubscript{3}O\textsubscript{4} and other conductive materials to anaerobic digesters for hydrogen sulfide (H\textsubscript{2}S) control reported S\textsuperscript{0} formation as the removal mechanism. This is a recent development. Most of the previous research has reported iron sulfide precipitation as the mechanism for H\textsubscript{2}S reduction when iron compounds were added to anaerobic digesters. This study, therefore, used a bioenergetics model to investigate if it is theoretically possible for S\textsuperscript{0} to form under AD conditions. Thermodynamics calculations revealed that it is possible for S\textsuperscript{0} to form in the AD environment. However, an electron shuttle, like magnetite, may be necessary to initiate this reaction.
PUBLIC ABSTRACT

Assessing the Role of Magnetite in Municipal Wastewater Treatment

Patricia Ayaa

Some municipal wastewater treatment (MWWT) facilities have adopted magnetite in their treatment processes through a technology called BioMag® to meet effluent regulatory requirements for total nitrogen and total phosphorus. However, there is limited information on the mechanisms and efficiency of magnetite in the removal of nitrogen (N) and phosphorus (P) from wastewater. This research, therefore, estimated its effectiveness in the removal of these nutrients, with a case study of the Marlay-Taylor Water Reclamation Facility in Maryland. The intervention analysis model was used, but a new forecasting approach to the model was proposed to fit the data in this study and other similar data. Results showed a significant improvement in both N and P removal. Graphical analyses showed an improvement in operating parameters like the mixed liquor suspended solids and sludge volume index. An account of the N and P removal mechanisms by the magnetite was also provided.

Some MWWT facilities using magnetite in their treatment process stabilize their waste sludge using anaerobic digestion (AD) and produce biogas. Therefore, laboratory studies were conducted to determine the effect of magnetite on biogas production (mainly methane and carbon dioxide) and on hydrogen sulfide (H₂S) gas reduction. Results showed no significant differences in biogas production, contrary to some studies which reported increases in methane yield with magnetite addition. H₂S in the biogas reduced below the concentration that is immediately dangerous to life and health (IDLH). An
increase in dissolved iron was also noted.

Some recent studies that used magnetite and other conductive materials in AD experiments reported elemental sulfur (S⁰) formation in the digesters. However, previous research that used iron compounds reported iron sulfide (FeS) formation as the mechanism of H₂S reduction. Therefore, a bioenergetics model was used to determine if the oxidation of H₂S to S⁰ is theoretically possible in the AD environment. S⁰ formation could also occur due to air presence or leakage in the digesters. Results showed that the reaction leading to S⁰ formation was exothermic, implying that energy was produced which could support microbial growth. However, conductive material may be required to initiate this reaction by facilitating electron transfer.
DEDICATION

I dedicate this dissertation to my parents, Mr. Isaac Kinyera and Mrs. Monica Kinyera, and to my brothers, Edward, Henry, and Paul, who have supported me throughout my education and life experiences and whose words have motivated and molded me into the person that I am today.
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Patricia Ayaa
# CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>iii</td>
</tr>
<tr>
<td>Public Abstract</td>
<td>v</td>
</tr>
<tr>
<td>Dedication</td>
<td>vii</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td>viii</td>
</tr>
<tr>
<td>List of Tables</td>
<td>xiii</td>
</tr>
<tr>
<td>List of Figures</td>
<td>xiv</td>
</tr>
<tr>
<td>Chapter</td>
<td></td>
</tr>
<tr>
<td>1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>References</td>
<td>7</td>
</tr>
<tr>
<td>2. Estimating the Effect of Magnetite on Nitrogen and Phosphorus Removal Using Intervention Analysis</td>
<td>9</td>
</tr>
<tr>
<td>Abstract</td>
<td>9</td>
</tr>
<tr>
<td>2.1. Introduction</td>
<td>9</td>
</tr>
<tr>
<td>2.2 Methodology</td>
<td>14</td>
</tr>
<tr>
<td>2.2.1 Data Acquisition and Selection</td>
<td>14</td>
</tr>
<tr>
<td>2.2.2 Data Inspection</td>
<td>15</td>
</tr>
<tr>
<td>2.2.3 Choice of Data Analysis Method</td>
<td>17</td>
</tr>
<tr>
<td>2.2.4 Intervention Analysis Model</td>
<td>17</td>
</tr>
<tr>
<td>2.2.5 Defining the Intervention</td>
<td>19</td>
</tr>
<tr>
<td>2.2.6 Statistical Analysis Procedures</td>
<td>20</td>
</tr>
<tr>
<td>2.3 Results and Discussion</td>
<td>22</td>
</tr>
<tr>
<td>2.3.1 Relationship Between the Influent and Effluent</td>
<td>22</td>
</tr>
<tr>
<td>2.3.2 Comparison of the Settling Characteristics Before and After the Technology Upgrade</td>
<td>24</td>
</tr>
<tr>
<td>2.3.3 Treatment of Flows Higher than the Design Capacity</td>
<td>25</td>
</tr>
<tr>
<td>2.3.4 Nitrogen Removal</td>
<td>28</td>
</tr>
<tr>
<td>2.3.5 Phosphorus Removal</td>
<td>36</td>
</tr>
</tbody>
</table>
4.3 Results and Discussion

4.3.1 Sulfur Formation ........................................................................................................ 105
4.3.2 Overall Energy Production ...................................................................................... 106
4.3.3 Cell Yield .................................................................................................................. 107

4.4 Conclusion and Significance ...................................................................................... 108
Data Availability Statement ............................................................................................. 111
Acknowledgments ............................................................................................................ 111
References ....................................................................................................................... 112

5. Summary, Conclusions, and Recommendations .......................................................... 116
References ....................................................................................................................... 123
Curriculum Vitae .............................................................................................................. 124
LIST OF TABLES

Table 2.1. WLAs and reported loadings taken from MDE (2018) and USEPA (2019), respectively .................................................................21

Table 2.2. Summary of results for TN .................................................................31

Table 2.3. Summary of results for TP .................................................................40

Table 3.1. Effect of Fe₃O₄ on methane production in anaerobic digestion ..................54

Table 3.2. Effect of Fe₃O₄ on sulfate reduction and H₂S production in anaerobic digestion ............................................................................................57

Table 3.3. Results from statistical intervention data analysis ..................................75

Table 4.1. Summary of results from the bioenergetics model ..................................108
LIST OF FIGURES

Fig. 2.1. Expected response of effluent TP and TN to the technology upgrade at the Marlay-Taylor facility.................................................................14

Fig. 2.2. Process flowchart for Marlay-Taylor WRF......................................................15

Fig. 2.3. Effluent versus influent TN. ...........................................................................23

Fig. 2.4. Effluent versus influent TP...........................................................................23

Fig. 2.5. Influent TN with error bars indicating the standard deviation. .........................23

Fig. 2.6. Influent TP with error bars indicating the standard deviation............................24

Fig. 2.7. Influent Q with error bars indicating the standard deviation...............................24

Fig. 2.8. SVI with error bars indicating the standard deviation.......................................25

Fig. 2.9. Effluent TN versus Q when Q > Q_{des} ............................................................26

Fig. 2.10. Effluent TP versus Q when Q > Q_{des} ...........................................................27

Fig. 2.11. SVI versus Q when Q > Q_{des} .....................................................................27

Fig. 2.12. Effluent TN with error bars indicating the standard deviation...........................28

Fig. 2.13. Model residuals for TN..................................................................................29

Fig. 2.14. Histograms and Q-Q plots for TN residuals....................................................29

Fig. 2.15. Lag plots for TN residuals.............................................................................30

Fig. 2.16. EWMA for TN for the forward prediction model............................................31

Fig. 2.17. MLSS with error bars indicating the standard deviation....................................34

Fig. 2.18. MLVSS with error bars indicating the standard deviation...............................34

Fig. 2.19. SRT with error bars indicating the standard deviation.......................................35

Fig. 2.20. Effluent TP with error bars indicating the standard deviation...........................36

Fig. 2.21. Model residuals for TP..................................................................................38
Fig. 2.22. Histograms and Q-Q plots for TN residuals.................................38
Fig. 2.23. Lag plots for TP residuals................................................................39
Fig. 2.24. EWMA for TP for the forward prediction model............................39
Fig. 2.25. Effluent TSS with error bars indicating the standard deviation..........42
Fig. 3.1. Anaerobic digester setup.................................................................60
Fig. 3.2. Magnetite solubility with (a) contact time; (b) magnetite dose; and
(c) mixing speed..........................................................................................67
Fig. 3.3. Color change in deionized water and precipitate due to magnetite........67
Fig. 3.4. (a) Effect of Fe$_3$O$_4$ addition on H$_2$S; (b) effect of FeCl$_2$ addition on H$_2$S;
(c) EWMA model for Fe; (d) EWMA model for H$_2$S; (e) model residuals for Fe;
and (f) model residuals for H$_2$S..................................................................69
Fig. 3.5. (a) Effect of Fe$_3$O$_4$ addition on gas volume; (b) effect of FeCl$_2$ addition on gas volume; (c) EWMA model for gas volume; and (d) model residuals for the gas volume.................................................................75
Fig. 3.6. (a) Effect of Fe$_3$O$_4$ addition on biogas composition; and (b) effect of FeCl$_2$
addition on biogas composition....................................................................78
Fig. 3.7. (a) Effect of Fe$_3$O$_4$ addition on CH$_4$ fraction; (b) effect of FeCl$_2$ addition on
CH$_4$ fraction; (c) EWMA model for CH$_4$; and (d) model residuals for CH$_4$ ........79
Fig. 3.8. (a) Effect of Fe$_3$O$_4$ addition on CO$_2$ fraction; (b) effect of FeCl$_2$ addition on
CO$_2$ fraction; (c) EWMA model for CO$_2$; and (d) model residuals for CO$_2$. ........79
Fig. 3.9. (a) Effect of Fe$_3$O$_4$ addition on N$_2$ fraction; (b) effect of FeCl$_2$ addition on
N$_2$ fraction; (c) EWMA model for N$_2$; and (d) model residuals for N$_2$. ............80
Fig. 3.10. O$_2$ in digester gas (a) when Fe$_3$O$_4$ was added to the reactor; and (b) when
FeCl$_2$ was added to the reactor...................................................................80
Fig. 4.1. Process flow chart for determining the Gibbs free energy for the overall
reaction and the microbial cell yield................................................................99
CHAPTER 1

INTRODUCTION

The wastewater treatment (WWT) industry is facing a challenge in meeting effluent regulatory requirements, mainly in terms of total nitrogen (TN) and total phosphorus (TP). This may be a result of aging infrastructure at some treatment facilities, old technology that does not target nutrient (nitrogen and phosphorus) removal, growing towns and populations which increase the loading at WWT facilities, more stringent nutrient effluent regulatory requirements imposed by regulatory authorities like the Environmental Protection Agency (EPA) and state regulatory agencies, among other reasons. Some of the sources of nitrogen (N) and phosphorus (P) in wastewater include human and animal waste, some soaps and detergents, and fertilizer from agricultural runoff. WWT facilities can be point sources of pollution to surface water bodies receiving their effluent discharge. When the effluent from these facilities contains high levels of N and P, this can lead to eutrophication in the water bodies which affects habitat for fish and other aquatic species, as well as human health, especially with instances like harmful algal blooms (USEPA 2017; NOAA 2018). To meet the challenge, some WWT facilities are adopting the use of BioMag®, a technology that adds magnetite to the biological WWT process to help the facilities meet the Waste Load Allocation (WLA) requirements for TN and TP stipulated in their National Pollutant Discharge Elimination System (NPDES) permits.

Magnetite is an iron ore mineral that occurs naturally in igneous, metamorphic, as well as sedimentary rocks (Nadoll et al. 2015), but can also be synthesized in the laboratory. It has a chemical formula of Fe₃O₄, and specific gravity of 5.2 (Perry et al.
1997). Its specific gravity is about five times that of water, which makes it attractive as ballast material in gravity separation applications such as in WWT, where it enables the treated sludge to settle faster in the final clarifiers at municipal wastewater treatment (MWWT) facilities (Evoqua 2017). Magnetite is ferrimagnetic and is therefore attracted to magnets and can easily be recovered from the settled sludge. The recovered magnetite can then be reused, which could help cut down procurement costs.

The use of magnetite in MWWT is a recent development that has garnered the attention of some WWT operators around the country. Through a technology called BioMag®, 10-15 micrometer-sized magnetite particles are added to the biological secondary WWT process to control the sludge blanket and speed up clarification of the sludge in the secondary clarifiers (Evoqua 2017). This enables higher surface loading rates and surface overflow rates and reduces the surface area requirement of the clarifiers, enabling facilities to operate in a smaller footprint (Evoqua 2017).

Recently, the City of Logan, Utah, decided to build a new mechanical WWT facility to enable the facility to meet new phosphorus and ammonia effluent limits imposed by the Utah Division of Water Quality (Carollo 2015). In assessing the alternatives, it was determined that a conventional WWT facility was the favorable choice. However, the land on which the facility was to be built could not support the size of the proposed facility (Carollo 2015). To solve this problem, they decided to adopt the BioMag® magnetite technology, as it would enable the facility to be built in a smaller footprint. This research was motivated by the decision by Logan City to adopt the BioMag® magnetite technology.
Discussions with some WWT operators who were also considering adding magnetite to their WWT processes to help them meet nutrient regulatory requirements revealed that there was some hesitancy in using the magnetite technology. This is because the technology is still relatively new, with only a few facilities using it. Also, at this time, the largest fully operational facility in the United States that had adopted this technology was the Marlay-Taylor Water Reclamation Facility (WRF) in Maryland, whose original design capacity was only 6 million gallons per day (MGD). Therefore, with a limited track record of the BioMag® technology, it is understandable why facilities 10 times or larger would hesitate to adopt this technology, especially since there were limited literature sources detailing magnetite use in MWWT and the mechanisms by which it works to remove N and P and help these facilities meet their nutrient removal goals.

As such, this research was conducted to investigate the efficiency of the magnetite-based technology in N and P removal and give an account of the potential nutrient removal mechanisms by the magnetite, so as to provide an additional information source that can help WWT operators make more informed decisions pertaining to the use of magnetite in MWWT and in downstream processes like anaerobic digestion (AD).

The first objective of this study, therefore, was to estimate the effect of magnetite on N and P removal at a MWWT facility. The Marlay-Taylor WRF in Maryland was used as a case study. A method called intervention analysis, developed by Box and Tiao (1965, 1975), was used to estimate the effect of the magnetite technology upgrade at the Marlay-Taylor facility. This method is used in time series forecasting to predict the time series before an intervention forward, and the time series after the intervention backward, and the difference between these forecasts is estimated as the effect of the intervention.
(Berthouex and Brown 2002; Box and Tiao 1965, 1975). The intervention in this case being the magnetite technology upgrade. This method is suitable for analyzing environmental data with serial correlation, and which does not have a constant mean or variance (Berthouex and Brown 2002; Box and Tiao 1965, 1975). A modified approach to the forecasting methodology in the intervention analysis model was however proposed to fit the data in this study and other similar data so as to obtain more realistic predictions. An account of the possible removal mechanisms of N and P by magnetite during MWWT was also provided. Graphical analysis was used to investigate the effect of the magnetite on operating parameters like the sludge volume index (SVI), mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS), and in treating wet weather flows that are higher than the design capacity of the facility. The information from the first objective is presented in Chapter 2 and has been published in the American Society of Civil Engineers’ (ASCE’s) Journal of Environmental Engineering (JEE).

The second objective was to investigate the effect of magnetite on the AD process. Because some facilities using magnetite in MWWT use AD to treat their waste sludge, this part of the study was aimed at investigating the effect of magnetite on the AD process in terms of biogas production and composition, and hydrogen sulfide (H₂S) gas production. Hydrogen sulfide is an undesirable component in biogas which can cause corrosion of metal and concrete components in the gas distribution system (USEPA 1991), shortening their lifespan, and can also be harmful to human health when exposed to the gas (OSHA 2020). Previous studies have used different size magnetite particles in AD experiments, some synthesized in the laboratory and others obtained commercially,
and yielded different results. For studies that reported a significant increase in methane production with magnetite addition (Suanon et al. 2016; Ajayi-Banji et al. 2021; Zhang et al. 2020), the increase was attributed to direct interspecies electron transfer (DIET) between exoelectrogenic bacteria and electrotrophic methanogens facilitated by the conductive magnetite particles. Other studies like Zhao et al. (2018) and Jung et al. (2020), however, did not observe a significant improvement in methane production. A study by Jung et al. (2020) observed a reduction in H₂S in solution and in the biogas and formation of elemental sulfur in the anaerobic digester, which was attributed to DIET between exoelectrogenic anaerobic sulfide oxidizing bacteria and electrotrophic methanogens, facilitated by the magnetite. Jin et al. (2019), however, observed an increase in the H₂S in solution, which could imply an increase in H₂S in the biogas.

This study therefore used the same magnetite supplied for use in the BioMag® process, in the same proportions of magnetite to suspended solids recommended for the BioMag® process, with the aim of producing results that would be similar to what would be observed at MWWT facilities using this technology. If there are benefits to the magnetite in the AD process, a recommendation will be made to recover the magnetite after AD instead of prior. This would help reduce the load on the magnetite recovery equipment and its lifespan, since AD is a sludge stabilization process that will reduce the quantities of sludge to be processed by the equipment. The solubility of magnetite and its potential implications on and beyond the AD process were also investigated. The information from this section is covered in Chapter 3 and has also been published in the ASCE’s Journal of Environmental Engineering.
The third objective of this study was to investigate whether it is theoretically possible for elemental sulfur ($S^0$) to form during AD without air/oxygen supplementation to the digester. A bioenergetics model was used. This investigation was sparked by recent studies that observed $S^0$ formation when they added conductive materials like magnetite to the AD process (Jung et al. 2020). Because addition of iron compounds has been popularly used as a method for reduction of hydrogen sulfide by precipitation of iron sulfide (FeS) in anaerobic digesters, this study aimed at investigating whether it is also theoretically possible to produce elemental $S^0$ instead of FeS during AD. This information is presented in Chapter 4. Note that FeS formation is a reduction process, while $S^0$ formation is an oxidation process. Also note that small amounts of air in the digester could lead to the oxidation of $H_2S$ to $S^0$, which is one of the methods used to reduce $H_2S$ in biogas (Saber and Takach 2009; Zafar 2020). Presence of air/oxygen in the digester could occur as a result of leakage of the air into the AD system or inadequate purging of air from containers used in AD experiments.

Chapter 5 provides a summary of the research in this dissertation, conclusions, and recommendations for future work.
References


CHAPTER 2

ESTIMATING THE EFFECT OF MAGNETITE ON NITROGEN AND PHOSPHORUS REMOVAL USING INTERVENTION ANALYSIS

Abstract

This study investigated the effectiveness of magnetite as ballast material through a technology called BioMag®, in nitrogen and phosphorus removal and in processing peak flows at a wastewater treatment plant, using data from Marlay-Taylor Water Reclamation Facility in Maryland. Using intervention analysis, the magnitude of the difference in effluent total nitrogen (TN) and total phosphorus (TP) before and after the magnetite technology retrofit was estimated, but with the time series forecast forward both before and after the upgrade, as opposed to a backward forecast of the series after the upgrade suggested by previous studies. The sludge volume index (SVI) and mixed liquor suspended solids (MLSS) were also examined to ascertain the effect of the magnetite technology on these parameters. Findings showed improved SVI and increased MLSS, and that the upgraded facility is successfully treating peak flows while maintaining good effluent quality. The effluent TN and TP decreased by 98% and 77%, respectively. These results were compared to results from a backward forecast, as well as results obtained from a simple difference between actual reported values.

2.1. Introduction

Nitrogen (N) and phosphorus (P) are nutrients of concern in receiving streams of effluent from wastewater treatment plants (WWTPs). Under the Clean Water Act (CWA), these nutrients are regulated by the United States Environmental Protection Agency (USEPA) through the National Pollutant Discharge Elimination System (NPDES) that issues effluent discharge permits to WWTPs (USEPA 2018). Therefore, it is imperative that the facilities comply with the waste load allocations (WLAs) they are assigned in order to avoid penalties (USEPA 2018), but most importantly, to protect the environment.

High concentrations of N and P in water bodies could cause excessive growth of algae, leading to eutrophication; impairing habitat for aquatic life, and consequently affecting human life through deterioration of the water quality (USEPA 2017). Excessive nutrients, especially P, may also result in harmful algal blooms (HABs) which are toxic to fish, birds, other aquatic animals, as well as humans; when they ingest, come in contact with, or eat fish from the tainted water (USEPA 2017; NOAA 2018). Due to impaired water clarity and aesthetics, these conditions could also affect tourism (USEPA Office of Water 2015).

With the undeniable increase in populations and industrial growth, many WWTPs are experiencing challenges meeting their NPDES permit limits for N and P discharge in the effluent. As a result, some facilities in the United States have adopted the use of magnetite as ballast material through BioMag® technology to improve their treatment processes (Evoqua 2018a). The technology is said to easily be retrofitted at existing activated sludge (AS) facilities without increasing the footprint of the facilities, improve
their nutrient removal capabilities, as well as increase the amount of wastewater treated per day (Evoqua 2015a). Some of the WWTPs that have adopted this technology include Marlay-Taylor (Evoqua 2018b), Conococheague, Smithsburg and Winebrenner in Maryland (Evoqua 2016a; Samovalov 2016); Sturbridge (Evoqua 2017a; Tighe & Bond 2018) and Marlborough Easterly in Massachusetts (Evoqua 2016b); Mystic in Connecticut (Karmasin et al. 2016); Upper Gwynedd Township in Pennsylvania (Evoqua 2017b) and Allenstown in New Hampshire (Clement and Irwin 2016).

Magnetite is an iron oxide mineral that occurs naturally in igneous, metamorphic as well as sedimentary rocks and has a chemical formula, Fe$_3$O$_4$ (Nadoll et al. 2015). The material is said to be inert under the conditions in WWTPs and hence would not degrade or react with other constituents in the wastewater (Evoqua 2017c). Magnetite also has ferrimagnetic characteristics (Maher 2007) which makes it easily recoverable from the wasted sludge using a magnet, and therefore, can be reused many times with minor losses of the material in the recovery process as it is separated from the wasted sludge (Evoqua 2015a). Recovery efficiencies over 95% have been reported (Evoqua 2015a). The material has a density of about 5,150 kg/m$^3$ and thus specific gravity of 5.15 (Engineering Toolbox 2009), which is about five times higher than that of water. Therefore, when it attaches to biological floc particles, which have a density of about 1,038 -1,065 kg/m$^3$ (Sears et al. 2006), the combined magnetite-floc particles will have higher densities and thus higher specific gravity than individual flocs, resulting in flocs with increased settling velocities once they reach the final clarifiers. The clarifiers would, therefore, work more effectively because of the increased densities of the particles (Sanin et al. 2011).
The significance of a higher settling velocity in the clarifiers can be explained using Eqs. (2.1) and (2.2), where $v$ = surface overflow rate in the clarifier; $V_i$ = settling velocity of the sludge-water interface measured in the first few minutes of the settleability test; $SF$ = factor of safety ranging from 1.75 to 2.5; and 24 = conversion factor from m/h to m/d (Metcalf and Eddy 2003).

$$v \left( \frac{m^3}{m^2 \times d} \right) = \frac{V_i \left( \frac{m^3}{m^2 \times h} \right) \times 24}{SF}$$

A higher surface overflow rate denoted by $v$ in m/s in Eq. (2.2) results in a higher volumetric flow rate ($Q$) and reduces the cross-sectional area requirement ($A$) of the clarifiers when $Q$ is kept constant or decreases. Hence, the magnetite ballast can enable WWTPs to increase their solids loading rates (SLRs) and allow larger volumes of wastewater than the original design flow capacities to be treated within the same footprint (Evoqua 2015a).

$$Q \left( \frac{m^3}{s} \right) = v \left( \frac{m}{s} \right) \times A(m^2)$$

The City of Logan, Utah, is in the process of upgrading its WWTP from a lagoon system to an AS system that will incorporate the BioMag® technology in order to meet new P and ammonia effluent limits imposed by the Utah Division of Water Quality (Carollo 2015). The City of Logan’s decision to adopt the magnetite-based technology is what inspired this research. The research was aimed at investigating the effectiveness of the magnetite in terms of biological nutrient removal, and in treating flows higher than the original design capacity of a WWTP, with a case study of the Marlay-Taylor Water
Reclamation Facility (WRF) in Maryland. The study involved examining whether the technology has made an impact on the effluent quality at the facility and quantifying this impact.

The impact was quantified using a method called intervention analysis which was originally developed by Box and Tiao (1965, 1975). The intervention model was, however, altered to fit the intervention in this study. Hence, the authors suggest an alternative approach in treating the data series after the intervention when the response to the intervention is as shown in Fig. 2.1; where point \( a \) represents the level of the time series right before the intervention, point \( b \) is the level after the full occurrence of the intervention and represents an immediate and permanent effect due to the intervention, and \( bc \) represents a small drift in the time series due to the system moving toward stability. The full effect of the intervention would be realized around point \( c \), and hence the observations toward \( c \) would be weighted higher than the observations toward \( b \). This approach is suggested when the drift in the time series before the intervention is minimal, and the expected effect of the intervention is immediate, as described by a step function (Box and Tiao 1975; Box et al 2008), implying that a larger drift in the series after the intervention is most likely as a result of the system trying to regain stability and hence the most recent observations, in this case, should be weighted higher to reflect the full effect of the intervention. Therefore, a forward forecast of the series after the intervention is proposed under these circumstances, as opposed to a backward forecast suggested by the original intervention model by Box and Tiao (1965, 1975).
2.2 Methodology

2.2.1 Data Acquisition and Selection

The data used was obtained from Marlay-Taylor WRF, located in St. Mary’s County, Maryland. The facility was upgraded to enhanced nutrient removal (ENR) status with BioMag® technology in order to meet their effluent total nitrogen (TN) and total phosphorus (TP) NPDES permit requirements (Evoqua 2018b). The upgraded facility uses a four-stage Bardenpho AS system, which is designed for N removal but also removes P (Metcalf and Eddy 2003). A flow chart of the facility’s treatment processes is shown in Fig. 2.2. The nutrient WLAs for Marlay-Taylor are 33,154 kg/year (73,093 lbm/year) for TN and 2,487 kg/year (5,482 lbm/year) for TP, measured according to EPA regulations in 40 CFR Part 136 (MDE 2018).

Time series data from the facility from 2012 to 2018 were examined and analyzed. The data were categorized into the (1) preupgrade period (2012-2013), (2) construction period (2014-2016), and (3) postupgrade period (2017-2018). The construction period is the period during which the facility was upgraded. Data from the pre- and postupgrade periods were analyzed both in Microsoft Excel and in R, while data
from the construction period were discarded. Before analysis in R, the data was cleaned by removing outliers and filling in the missing values using the function `tsclean()` (Dalinina 2017).

![Fig. 2.2. Process flowchart for Marlay-Taylor WRF.](image)

2.2.2 Data Inspection

The preupgrade data were examined to determine if there was a relationship between the influent and effluent TN and TP concentrations. If a relationship existed, it would require that the data be further analyzed to determine whether the influent TN and TP concentrations had changed significantly since upgrading the facility. The reason for this analysis was to ascertain whether any differences that may be seen between the preupgrade and postupgrade effluent would be due to the technology upgrade or due to changes in the influent concentrations.

The sludge volume index (SVI) was examined to ascertain if this parameter had improved since upgrading the facility. SVI is an important parameter used to determine how well the sludge will settle in the clarifier in terms of compaction of the solids and
clarification of the effluent (Metcalf and Eddy 2003). According to IEPA (1997), an SVI of about 50 mL/g indicates a sludge that settles very well while sludges with an SVI above 120 mL/g settle poorly. Therefore, in this study, 120 mL/g was adopted as the desired SVI value. Sludges with an SVI above 150 mL/g have been linked with filamentous microorganisms which would hinder sludge settling in the clarifiers (Metcalf and Eddy 2003). This analysis was necessary because, as earlier mentioned, magnetite has a specific gravity about five times that of a biological floc and is therefore expected to increase the settling velocities of the flocs and thickening of the sludge in the clarifiers due to its weight (Evoqua 2017c), thereby improving the SVI.

If the sludge settling velocity is increased, this should increase the surface overflow rate and in turn increase the flow rate, \( Q \), as was shown in Eqs. (2.1) and (2.2). This means that the upgraded facility should be able to process higher flows than its original intended design capacity \( Q_{des} \). The effluent TN and TP were therefore compared before and after the technology upgrade on days when the flow exceeded its design capacity to check for the facility’s effectiveness in nitrogen and phosphorus removal during high flow events. Comparisons of the SVI were also made to see how the settling characteristics of the sludge were affected by the high flows.

As the mixed liquor suspended solids (MLSS) concentration is an important operating parameter in an AS system, it was important to see how the magnetite technology has affected this parameter since upgrading the facility. A MLSS of 3000-4000 mg/L is desired for a four-stage Bardenpho AS system (Metcalf and Eddy 2003), which is the configuration of the Marlay-Taylor facility.
2.2.3 Choice of Data Analysis Method

The effluent data were analyzed to determine if there has been an improvement in effluent quality since the facility upgrade and if the magnetite technology has enabled the facility to meet its NPDES WLA requirements for TN and TP. The difference in effluent TN and TP since the upgrade was estimated using a method called intervention analysis, which was originally developed by Box and Tiao (1965, 1975). The t-test or ANOVA tests were not ideal for the analysis because the data were not normally distributed, did not satisfy the requirement of constant variance, and because most time series data is believed to have serial correlation which renders these tests unsuitable (Box and Tiao 1965, 1975; Booman et al. 1986; Berthouex and Brown 1994, 2002).

2.2.4 Intervention Analysis Model

Intervention analysis is used in time series analysis to estimate the magnitude of the change in a time series due to some kind of intervention when the data are serially correlated (Box and Tiao 1965, 1975). The intervention in this study is the magnetite technology retrofit at the Marlay-Taylor facility. The method is suitable for time series data which can be defined as nonstationary, i.e. time series that do not have a constant mean or variance (Box and Tiao 1965, 1975); and employs the white noise-random walk model which accounts for random noise as well as random drift in a time series (Pallesen et al. 1985; Booman et al. 1986; Berthouex and Brown 1994, 2002).

The white noise-random walk model is essentially the same as an ARIMA (0, 1, 1) model (Pallesen et al. 1985; Berthouex and Brown 1994, 2002). ARIMA models are generally used in time series forecasting. The model can be defined by Eq. (2.3)
\[ y_t = y_{t-1} + a_t - \theta a_{t-1} \]  

where \( y_t \) = the observed value of the variable at a specified time, \( t \); \( \theta \) = weighting factor for the moving average and ranges anywhere from 0 to 1; and \( a_t \) = independent random noise variable that is normally distributed with a mean of 0 and variance \( \sigma_a^2 \) (Pallesen et al. 1985; Berthouex and Brown 2002). A \( \theta \) value of 0 would indicate a stationary time series with no drift, and all the observations in the series would carry equal weight and would all be used in making the forecast (Berthouex and Brown 2002). Therefore, a \( \theta \) value that approaches 0 would mean that there is a slow drift in the time series and the series approaches stationarity, in which case most of the observations in the series would be used in estimating the intervention effect (Berthouex and Brown 2002). Conversely, when \( \theta \) approaches 1, this would mean that the series drifts rapidly and fewer observations closer to the intervention would be used to estimate its effect (Berthouex and Brown 2002).

Because the ARIMA (0,1,1) model is similar to an exponentially weighted moving average (EWMA) model, the EWMA can be used to forecast the time series (Berthouex and Brown 2002). The model is used to predict forward from the data series before the intervention and predict backward from the data series after the intervention; giving the observations closer to the intervention a higher weight than observations further away, with the magnitude of the difference between the two predicted values being the effect caused by the intervention (Box and Tiao 1965; Pallesen et al. 1985; Berthouex and Brown 1994, 2002). The data series are weighted in this way in order to minimize the influence of random drift or trends on the results obtained from the model (Pallesen et al. 1985).
2.2.5 Defining the Intervention

Box and Tiao (1975) and Box et al. (2008) describe different ways in which a time series might behave after an intervention, basing on whether the intervention event is defined by a step function or a pulse function. A step function is one for which the effects of the intervention would remain permanently, while for a pulse function, the effects would be temporary with the time series returning to its level right before the intervention but may leave some residual effect (Box and Tiao 1975; Box et al. 2008).

In this study, the BioMag® intervention at the Marlay-Taylor facility is defined by a step function, as the nature of this intervention is such that it is a modification to the system, and its effect is expected to be permanent, and not temporary such that the effect diminishes with time, as or after it is withdrawn from the system. The response of the system to this intervention was defined as an instant step decrease in the TN and TP levels followed by a gradual decrease to a more constant level as was illustrated in Fig. 2.1, to account for operator familiarity with the new technology. This decision was based on the notion that with a new technology, the operators of the technology may take some time to acclimate to the change and thus operate more efficiently with time. As such, it is expected that the most recent observations after the upgrade would be a better reflection of the fuller effect of the new technology.

Therefore instead of randomly selecting a transition period, which in this study would be the time it would take for the system to stabilize as the operators master the operation of the new technology, and predicting backward to this point like it was done in previous studies like Pallesen et al. (1985), Booman et al. (1986), and Berthouex and Brown (1994, 2002); the authors predicted the data series after the upgrade forward such
that the most recent observations carried a higher weight than the observations immediately after the upgrade. Randomly selecting a transition period and predicting backward would give the data at the end of the transition period a higher weight than the data at the end of the time series, therefore if a transition period is inaccurately selected, this would affect the forecast result. On the other hand, forecasting the time series forward would ensure that the full effect of the intervention is accounted for, and if the series has a slow drift and tends towards stationarity, this drift could be assumed to be insignificant and hence ignored, depending on how it would impact future decisions.

2.2.6 Statistical Analysis Procedures

The data analysis in this study followed the procedure by Berthouex and Brown (2002) using code from Stevens (Personal communication, 2018) that was written in R. First, the moving average parameter, $\theta$, was estimated for the preupgrade period ($\theta_{pre}$), and then for the postupgrade period ($\theta_{post}$), using the R function `arima()` (Berthouex and Brown 2002). This was followed by estimation of a $\theta$ value that would give the best prediction over the entire dataset, minimizing the sum of squares in the two periods, by iteration and using the R function `optim()`. After optimizing the value of $\theta$, it was used to predict the next values forward from before and after the upgrade using the EWMA. The magnitude of the effect of the technology upgrade was then calculated as the difference between the two predictions. This result was termed the forward prediction.

The variance of the estimated shift ($Var(\delta)$) was calculated using Eq. (2.4), where $\sigma_e^2 = \text{variance of the error from white noise}$; $\sigma_e^2 = \text{variance of the error due to random drift}$, and $G = \text{period within which the intervention is realized}$ (Pallesen et al. 1985; Berthouex and Brown 2002).
\[ Var(\delta) = 2(1 - \theta)\sigma^2_e + G\sigma^2_e \] (2.4)

A second analysis was done using intervention analysis, but this time predicting backward the time series after the intervention, as suggested by studies previously cited, and the result from this was termed the **backward prediction**.

Finally, a third result, which is the difference between the preupgrade and postupgrade periods from the reported data given in Table 2.1 (USEPA 2019), was obtained by first calculating the average in each period and then obtaining the difference between the two. This result was termed the **simple difference**.

A comparison of the results from the forward prediction, the backward prediction, and the simple difference, was made to ascertain the difference between the three approaches, with the implication of each result. However, the conclusion for this study was based on the forward prediction.

Table 2.1. WLAs and reported loadings taken from MDE (2018) and USEPA (2019), respectively

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>WLA</th>
<th>2012</th>
<th>2013</th>
<th>2017</th>
<th>2018</th>
</tr>
</thead>
<tbody>
<tr>
<td>TN</td>
<td>kg/year</td>
<td>33,154</td>
<td>67,211</td>
<td>82,571</td>
<td>12,923</td>
<td>11,822</td>
</tr>
<tr>
<td></td>
<td>lbm/year</td>
<td>73,093</td>
<td>148,175</td>
<td>182,039</td>
<td>28,491</td>
<td>26,064</td>
</tr>
<tr>
<td>TP</td>
<td>kg/year</td>
<td>2,487</td>
<td>4,862</td>
<td>4,460</td>
<td>1,641</td>
<td>1,432</td>
</tr>
<tr>
<td></td>
<td>lbm/year</td>
<td>5,482</td>
<td>10,718</td>
<td>9,832</td>
<td>3,618</td>
<td>3,156</td>
</tr>
</tbody>
</table>
2.3 Results and Discussion

2.3.1 Relationship Between the Influent and Effluent

Figs. 2.3 and 2.4 show that there is no linear correlation between the influent and effluent TN and TP, respectively, during the preupgrade period. The coefficients of determination, $R^2$, for TN and TP were 0.029 and 0.001, respectively. This means that the variation in the effluent TN or TP cannot be explained by the linear regression model. Thus, the level of nutrient removal achieved in the effluent cannot be predicted based on the influent, within the domain of influent loadings received at this facility, as shown in Figs. 2.3 and 2.4, where similar effluent quality was attained across the range of influent TN and TP loadings received. The levels of effluent TN and TP achieved were therefore assumed to be solely a result of the effectiveness of the N and P removal processes at this treatment facility. Thus, if a difference in magnitude is seen between the preupgrade and postupgrade effluent, it is most likely due to changes in the design and operating parameters at the facility stemming from the technology upgrade that affect the N and P removal processes. In any case, a comparison of the influent TN and TP in Figs. 2.5 and 2.6, respectively, before and after the upgrade shows that there were no large differences in variation between the two periods that should significantly affect their levels in the effluent, as shown by the overlapping error bars. The influent flow, $Q$, also did not show a large variation between the two periods as seen in Fig. 2.7 and thus was not considered a possible cause of any changes that might be seen in the effluent quality. It is important to note that the deductions made in this section were based on the data from this study and may or may not apply to other facilities.
Fig. 2.3. Effluent versus influent TN.

Fig. 2.4. Effluent versus influent TP.

Fig. 2.5. Influent TN with error bars indicating the standard deviation.
Fig. 2.6. Influent TP with error bars indicating the standard deviation.

Fig. 2.7. Influent Q with error bars indicating the standard deviation.

2.3.2 Comparison of the Settling Characteristics Before and After the Technology Upgrade

Fig. 2.8 shows the monthly average SVI values in the preupgrade and postupgrade periods. The postupgrade SVI values were generally much lower than the preupgrade values and within the desired limit of 120 mL/g, with most of the months having an SVI closer to 50 mL/g, implying very good sludge settling ability (IEPA 1997). The preupgrade SVI values, however, were greater than 120 mL/g; going as high as 450 mL/g.
in April 2013, indicating that the sludge had poor settling characteristics before the upgrade. Fig. 2.8 also shows that while there was high variability in the SVI before the upgrade, the variability became less conspicuous after the upgrade. It can therefore be inferred from this data that the magnetite technology has improved the sludge settling characteristics at the facility, with the SVI becoming more stable and staying within the desired limits.

Other BioMag® retrofitted WWTPs like Sturbridge in Massachusetts managed to achieve an SVI of less than 40 mL/g (Evoqua 2017a), and Mystic in Stonington, Connecticut, managed to reduce the SVI from about 275 mL/g to 104 mL/g (Karmasin et al. 2016), consistent with the results at the Marlay-Taylor plant.

2.3.3 Treatment of Flows Higher than the Design Capacity

The Marlay-Taylor WRF was originally designed to treat a maximum flow of 22,712 m³/day (6 MGD) (Evoqua 2018b). The data presented in this section is from days when the design flow, \(Q_{des}\), was exceeded. Hence, the effluent TN, effluent TP and SVI
were plotted verses the flow, $Q$, to ascertain the difference, if any, in the behavior of these parameters when the design flow capacity was exceeded.

Figs. 2.9 and 2.10 show that the effluent TN and TP, respectively, were generally lower in the postupgrade period than in the preupgrade period despite $Q_{des}$ having been exceeded. Fig. 2.11 shows that the SVI was much lower in the postupgrade period, with values generally closer to 50 mL/g indicating sludges with very good settling characteristics, unlike in the preupgrade period that had values higher than 150 mL/g indicating poor settling sludges (IEPA 1997).

It is therefore evident from this data that the upgraded facility is producing good quality effluent even when the design flow is exceeded, unlike previously, and this implies an increase in the facility’s treatment capacity in terms of nitrogen and phosphorus removal.

![Graph showing effluent TN versus Q when Q > Q_{des}](image)

Fig. 2.9. Effluent TN versus Q when $Q > Q_{des}$. 
Fig. 2.10. Effluent TP versus Q when $Q > Q_{des}$. 

Fig. 2.11. SVI versus Q when $Q > Q_{des}$. 
2.3.4 Nitrogen Removal

Effluent nitrogen regulations at the Marlay-Taylor WRF are based on TN, with the WLA equal to 33,154 kg/year (73,093 lbm/year) (Table 2.1), and the target monthly mean concentration limit equal to 4 mg/L (MDE 2018). Fig. 2.12 shows that the postupgrade concentrations were generally below the 4 mg/L target, except for January 2018, which was only slightly higher, at 4.5 mg/L. The preupgrade concentrations, however, exceeded the 4 mg/L limit by up to four times in some of the months, with the lowest month almost two times the target.

![Fig. 2.12. Effluent TN with error bars indicating the standard deviation.](image)

The magnitude of the difference seen between the preupgrade and postupgrade TN was estimated using intervention analysis, by using the EWMA model to predict the next values in the preupgrade and postupgrade time series. To establish if the model used was a good fit for the data, the model residuals were plotted in Fig. 2.13, and they show a random pattern, implying that the linear model of the EWMA fits the data (Stat Trek 2019). Histograms and Q-Q plots for the preupgrade and postupgrade TN residuals are also plotted in Fig. 2.14, and they show approximate normal distributions, while the lag
plots in Fig. 2.15 indicate that the residuals were independently distributed. Therefore, the EWMA model was a good fit for the data. Note that this applies to both the forward and backward predictions as the same data were used.

Fig. 2.13. Model residuals for TN.

Fig. 2.14. Histograms and Q-Q plots for TN residuals.
With the forward prediction, the EWMA in Fig. 2.16 was used to predict the next values forward for both the preupgrade and postupgrade series with the overall moving average parameter, $\theta$, equal to 0.208. The preupgrade and postupgrade TN predictions made were 171.3 kg/day and 3.8 kg/day, respectively. Hence the difference in TN between the two periods, $\delta$, was 167.5 kg/day, with a standard deviation of 9.1 kg/day. This gives a reduction in annual TN, $\Delta$, of 61,141 kg/year, a 98% decrease, which is almost two times the WLA for TN. A summary of these results is presented in Table 2.2.
Fig. 2.16. EWMA for TN for the forward prediction model.

Table 2.2. Summary of results for TN

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Simple difference</th>
<th>Forward prediction</th>
<th>Backward prediction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_{pre}$</td>
<td>-</td>
<td>0.013</td>
<td>0.013</td>
</tr>
<tr>
<td>$\theta_{post}$</td>
<td>-</td>
<td>0.331</td>
<td>0.331</td>
</tr>
<tr>
<td>$\theta$</td>
<td>-</td>
<td>0.208</td>
<td>0.208</td>
</tr>
</tbody>
</table>

Preupgrade prediction

- kg/d: - 171.3 171.3
- lbm/d: - 377.6 377.6

Postupgrade prediction

- kg/d: - 3.8 29.6
- lbm/d: - 8.3 65.2

$\delta$

- kg/d: - 167.5 141.7
- lbm/d: - 369.3 312.4

Standard deviation

- kg/d: - 9.1 25.6
- lbm/d: - 20.2 56.5

$\Delta$

- kg/yr: 62,518 61,141 51,716
- lbm/yr: 137,829 134,792 114,014

Note: $\theta_{pre}$ = moving average parameter for the preupgrade time series; $\theta_{post}$ = moving average parameter for the postupgrade time series; $\theta$ = overall moving average parameter for the entire data set; $\delta$ = reduction in TN, per day; $\Delta$ = annual reduction in TN.

With the backward prediction, the value of $\theta$ was the same as that obtained for the forward prediction. The results from the backward prediction are also shown in Table 2.2
and indicate a reduction in TN of 141.7 kg/day with a standard deviation of 25.6 kg/day. This gives an annual reduction of 51,716 kg/year, an 84% decrease in the effluent TN.

The estimate from the forward prediction was 9,425 kg/year lower than that from the backward prediction, hence the estimated reduction of TN from the backward prediction was 14% less than that from the forward prediction.

With the simple difference approach, the average pre- and postupgrade TN calculated from reported annual TN loadings shown in Table 2.1 (USEPA 2019), were 74,891 kg/year and 12,373 kg/year, respectively, resulting in a difference of 62,518 kg/year: an 83% reduction in TN. The results are given in Table 2.2.

The simple difference assumes that all observations equally contribute to the estimated level of the data series before and after the intervention, as explained by the white noise model (Pallesen et al. 1985; Berthouex and Brown 2002). However, the moving average parameter for the data series, $\theta$, was estimated to be 0.208, implying some drift in the series that needs to be accounted for. Therefore, the simple difference does not give a proper estimate of the intervention effect as it gives equal weight to the data immediately after the intervention which is still in transition and does not reflect the full effect of the intervention, as well as data further away from the onset of the intervention which does not represent the level of the time series right before the intervention.

The estimated moving average parameters for the preupgrade and postupgrade periods, $\theta_{\text{pre}}$ and $\theta_{\text{post}}$, were 0.013 and 0.331, respectively (Table 2.2). This indicates that the effluent TN series barely drifted before the intervention, while after the intervention, there was an increase in the drift. Hence the increase in drift was believed to be due to the
operators getting acquainted with the new technology and thus achieving better effluent quality with time. The overall $\theta$ of 0.208 used in weighting the observations was also low, implying that the series were tending towards stationarity and hence most of the observations would be used in making the forecasts. As such, the estimated effect of the intervention, $\Delta$, is expected to be close to the result from the simple difference approach. Looking at the results in Table 2.2, the forward prediction result is closer to the simple difference result than the backward prediction result. Therefore, with these postulations together with the assertion that the effect of the technology upgrade should be permanent and not wane with time, the authors believe that the forward prediction is justified and will give the most reasonable estimate of the intervention effect compared to the backward prediction and simple difference approaches.

The mechanism of enhanced nitrogen removal with the magnetite technology can be explained as follows: the high density of magnetite enables a more thickened settled sludge in the final clarifiers, and a more thickened sludge would mean higher MLSS (Evoqua 2015a) in the return AS (RAS) and thus higher mixed liquor volatile suspended solids (MLVSS) in the bioreactor. Higher MLVSS would imply a higher microbial population, which includes nitrifiers and denitrifiers, which would improve nitrogen removal. An MLSS concentration of about 3000-4000 mg/L is desired for a four-stage Bardenpho bioreactor process (Metcalf and Eddy 2003), which is the configuration of the reactors at the Marlay-Taylor facility.

Fig. 2.17 shows that generally, the MLSS fell short of the requirement in the preupgrade period, while in the postupgrade period, the MLSS was almost double the requirement. As MLVSS is an approximate measure of the active biomass (the microbes)
in the system, which treat the wastewater, it was important to see how the microbial population was increased in the postupgrade period. Fig. 2.18 shows an increase in the MLVSS, implying an increase in the nitrifying and denitrifying bacteria in the bioreactor, which will enhance nitrogen removal.

![Fig. 2.17. MLSS with error bars indicating the standard deviation.](image1)

![Fig. 2.18. MLVSS with error bars indicating the standard deviation.](image2)

As longer solids retention times (SRTs) may improve nitrification in the system (Metcalf and Eddy 2003), the preupgrade and postupgrade SRTs were compared to
establish whether the reason for lower effluent TN was due to an increase in SRTs in the postupgrade period. As seen in Fig. 2.19, this was not the case. Fig. 2.19 was compared with Fig. 2.12 to establish if increased SRTs correlated with lower effluent TN. This also did not hold, and this is probably because nitrogen removal is not solely based on SRTs.

![SRT with error bars indicating the standard deviation.](image)

The results from this section show that the technology upgrade has helped the Marlay-Taylor WRF to considerably improve the nitrogen removal process, which has enabled the facility to meet its WLA requirements for TN, as seen in Table 2.1.

Other wastewater treatment plants like Mystic in Stonington, Connecticut, also incorporated BioMag® technology in order to meet their annual effluent TN requirement of 5.2 mg/L (Karmasin et al. 2016). The facility was able to reduce effluent TN by 80% and earn a credit from the Connecticut Department of Energy and Environmental Protection (Town of Stonington WPCA Board 2015). Smithsburg WWTP in Maryland also adopted the technology in order to meet their new NPDES permit limits of 3.9 mg/L NH₃-N in the winter and 2.3 mg/L in the summer (Evoqua 2015b). With the technology upgrade, the facility was able to improve its settling and nitrification problems, and
consequently reduce NH$_3$-N to about 0.34 mg/L, a value much lower than the winter regulatory requirement of 3.9 mg/L (Evoqua 2015b).

2.3.5 Phosphorus Removal

The WLA for TP at the Marlay-Taylor WRF is 2,487 kg/year (5,482 lbm/year) (Table 2.1), with the target monthly mean concentration limit equal to 0.3 mg/L (MDE 2018). Fig. 2.20, shows that the postupgrade effluent concentrations were generally lower than the target limit of 0.3 mg/L, with a few months going slightly above it, while the preupgrade concentrations were generally higher than 0.3 mg/L with a few months meeting the requirement. Note that the November 2017 average of 1.4 mg/L was omitted because the chemical feed for additional phosphorus removal was offline for a few days during the month, making the monthly average TP much higher than in the rest of the months (M. O’Dell, personal communication, 2018).

![Graph showing effluent TP concentrations with error bars indicating the standard deviation.](image)

Fig. 2.20. Effluent TP with error bars indicating the standard deviation.

As with the TN analysis, the EWMA model was used to estimate the magnitude of the difference in effluent TP between the preupgrade and postupgrade periods. The
model residuals were plotted in Fig. 2.21, and they indicate a random distribution; the histograms and Q-Q plots of the residuals were plotted in Fig. 2.22, and they indicate that the data were approximately normally distributed; while the lag plots of the residuals were plotted in Fig. 2.23 and indicate that the residuals were independently distributed. Therefore, the EWMA model was a good fit for the data. Also, note that these plots apply to both the forward and backward predictions.

With the forward prediction, the EWMA model in Fig. 2.24 was used to forecast the data series before and after the upgrade with an overall moving average parameter, $\theta$, of 0.306. The preupgrade and postupgrade predictions were 11.1 kg/day and 2.5 kg/day, respectively. Therefore, the estimated difference in TP loading between the two periods, $\delta$, was 8.6 kg/day, with a standard deviation of 2.2 kg/day, and the estimated annual difference, $\Delta$, equal to 3,131 kg/year. This gives a 77% reduction in effluent TP, which is more than the facility’s WLA for TP. A summary of these results is shown in Table 2.3.

With the backward prediction, $\theta$ was also equal to 0.306, and the estimated difference in TP equal to 8.9 kg/day with a standard deviation of 2.0 kg/day. The estimated annual difference was thus 3,265 kg/year, an 81% reduction in TP. The results are shown in Table 2.3. The estimated reduction from the backward prediction was 134 kg/year more than that from the forward forecast: a further 4% decrease in the effluent TP than the estimate from the forward prediction.

With the simple difference approach, the preupgrade and postupgrade estimates for TP calculated from the data in Table 2.1 were 4,661 kg/year and 1,536 kg/year, respectively. This gives a difference of 3,125 kg/year, a 67% reduction in effluent TP.
Fig. 2.21. Model residuals for TP.

Fig. 2.22. Histograms and Q-Q plots for TN residuals.
Fig. 2.23. Lag plots for TP residuals.

Fig. 2.24. EWMA for TP for the forward prediction model.
The estimated moving average parameters, $\theta_{\text{pre}}$ and $\theta_{\text{post}}$, were 0.257 and 0.371, respectively (Table 2.3), indicating that the drift in the effluent TP series before the intervention was slightly lower than the drift in the data series after the intervention. This increase in drift was also believed to be due to operator familiarity with the new technology resulting in better quality effluent with time. The estimated reduction in TP, $\Delta$, for the forward prediction was very close to the estimate from the simple difference, but the difference was larger with the backward prediction as seen in Table 2.3. As explained in the TN discussion, the forward prediction results were believed to be a better estimate of the intervention effect than the backward prediction and simple difference results.
The mechanism of enhanced P removal at Marlay-Taylor could be explained by (1) an increase in MLVSS in the bioreactor (shown in Fig. 2.18) due to better compaction of the sludge at the bottom of the clarifier by the magnetite, which would increase the polyphosphate accumulating organisms (PAOs) in the RAS that take up P (Metcalf and Eddy 2003); (2) the addition of a carbon source to the second anoxic zone (M. O’Dell, personal communication, 2018) to provide food for the PAOs to grow and hence increase their capacity for P uptake in the final aerobic zone (Metcalf and Eddy 2003); (3) enhanced clarification as more of the P tied to the total suspended solids (TSS) settles out to the bottom of the clarifier thus decreasing the amount of P in the effluent (Metcalf and Eddy 2003); and (4) due to chemical addition of ferric chloride for additional P removal. Steps (1) and (2) both increase P uptake by the PAOs, and removal is achieved by wasting the PAOs through the waste activated sludge stream (Metcalf and Eddy 2003). To establish if there was an improvement in clarification since the upgrade, to justify step (3), a comparison of the effluent TSS before and after the technology upgrade was made and is shown in Fig. 2.25. The figure shows that there was a general decrease in the effluent TSS after the upgrade which could be attributed to increased settling rates and better clarification by the magnetite.

Therefore, because the four-stage Bardenpho AS system configuration that is used at the Marlay-Taylor WRF is tailored to N removal and not so much for P removal (Metcalf and Eddy 2003), it can be concluded that the increase in P removal at the facility is due to a combination of biological and physical removal enhanced by the magnetite, as well as chemical removal by the addition of ferric chloride. A three-stage or five-stage Bardenpho system designed for biological removal of both nitrogen and
phosphorus could probably have helped eliminate the chemical addition step for additional P removal and offset the cost of the chemicals. Nevertheless, the upgraded facility has managed to improve P removal, and the facility is now able to meet their WLA for TP, as seen in Table 2.1.

![Effluent TSS with error bars indicating the standard deviation.](image)

Fig. 2.25. Effluent TSS with error bars indicating the standard deviation.

Other facilities, such as Upper Gwynedd Township WWTP adopted BioMag® technology in order to meet an expected future effluent TP limit of 0.2 mg/L (Evoqua 2017b). The facility was having problems treating peak wet weather flows, with solids settling problems in the clarifiers (Evoqua 2017b). After upgrading the facility, it was able to meet its effluent TP permit limit of 0.2 mg/L as well as increase its peak design flow from 12 MGD to 22.5 MGD (Evoqua 2017b). Marlborough Easterly WWTP in Massachusetts was also able to meet its new effluent TP limit in the summertime of 0.1 mg/L, and an average effluent TP of 0.06 mg/L after upgrading the facility (Evoqua 2016b).
2.4 Conclusion

Intervention analysis was used to estimate the magnitude of the effect of magnetite, which has been packaged in a technology called BioMag®, on the effluent TN and TP at Marlay-Taylor Water Reclamation Facility in Maryland. A forward forecast of the data series after the intervention is proposed when the preintervention time series has minimal drift and the postintervention time series has a larger drift indicated by an immediate permanent step change followed by a gradual decrease or increase to system stability. The forward forecast as such assumes the most recent observations to constitute the fuller effect of the intervention and therefore assigns higher weights to these observations and lesser weights to those closer to the intervention when the plant and staff are still in transition. This approach is a bit different from previous studies which suggested that the data closer in time to the intervention should be more relevant and should carry more weight than data further away, and hence made a backward forecast of the postintervention series.

With the proposed approach, the reduction in TN was about 98% and 77% for TP. In comparing these results with those from the backward prediction and simple difference, the results from the forward prediction compared more closely with those from the simple difference than the backward prediction. Hence the forward prediction results were assumed more reasonable estimates as the moving average parameters seemed to indicate that the time series were tending towards stationarity, and therefore, the expected results should be closer in value to the results from the simple difference. While the reduction in TN can be assumed to be entirely due to incorporation of magnetite, the reduction in TP could also be attributed to chemical
removal using ferric chloride, and addition of a carbon source to feed the microbes, which were not used before the upgrade.

Findings also indicated that Marlay-Taylor has been meeting its WLA requirements since the upgrade, and the facility has managed to maintain desired SVI and MLSS values and successfully treat larger flows than its original design capacity, while still meeting the effluent nutrient regulatory requirements.

For the data analysis, the authors suggest that before applying the forecasting model, it is important for one to study their system carefully and model the anticipated effects of their specific intervention in order to determine whether to predict forward or backward to obtain more realistic estimates, as small differences in predictions can in some cases lead to significantly greater implementation costs.

The information in this study could be helpful to wastewater treatment facilities struggling to meet their WLA requirements for TN and TP, and it could help planners/modelers to cogitate about tailoring the intervention model to their specific interventions so as to obtain better predictions, and consequently make better decisions. In addition, the information could encourage researchers to look into other materials or technologies that might provide similar or additional benefits that could save facilities money by eliminating the need to build entirely new facilities.

Data Availability Statement

Some or all data, models, or code that support the findings of this study are available from the corresponding author upon reasonable request.
Acknowledgments

The authors would like to thank the Utah Water Research Laboratory (UWRL) for providing funding that enabled this research; Mr. Issa Hamud and the City of Logan for their support and accommodation in meetings discussing the proposed BioMag® wastewater treatment facility in Logan, UT; Mr. Nathan Antonneau of Evoqua Water Technologies for his role and cooperation in ensuring that the authors obtained the information that was essential to this research; and Mr. Morgan O’Dell, Mr. DuWayne Potter, and the entire staff at Marlay-Taylor WRF in Maryland for their cooperation, and for providing the data that was used in this research.
References


CHAPTER 3

EFFECT OF MAGNETITE ON ANAEROBIC DIGESTER BIOGAS, HYDROGEN SULFIDE GAS, DIGESTER EFFLUENT AND RELATED PROCESSES

Abstract

Some wastewater treatment (WWT) facilities are using magnetite in their treatment process, through a technology called BioMag®, and stabilizing their wasted sludge using anaerobic digestion (AD) after recovering most of the magnetite for reuse. This research investigated whether this magnetite would benefit the AD process to assess the possibility of magnetite recovery after AD as this could reduce the loading on the recovery equipment as well as operation and maintenance costs of magnetite recovery due to decreased sludge quantities. Because some conflicting results were seen from previous studies, which could be due to particle size, or stability as some studies used synthesized magnetite particles that can be unstable, which may affect the properties and behavior of the magnetite, this study used the same magnetite supplied for the BioMag® process. The effect of this magnetite on biogas production, biogas composition, hydrogen sulfide gas (H₂S) reduction, and digester effluent were investigated. Results showed an increase in the effluent dissolved iron and a 49% reduction in H₂S. No considerable effect was seen on the gas volume and composition.

3.1 Introduction

Some municipal biological wastewater treatment (WWT) facilities are adopting magnetite (Fe₃O₄) in their secondary WWT processes, through a technology called BioMag® (Evoqua Water Technologies, Pittsburgh), to improve efficiency and enable them to meet their waste load allocation (WLA) requirements (Ayaa et al. 2020; Evoqua Water Technologies 2020). A large percentage of the Fe₃O₄ is recovered from the wasted sludge/waste activated sludge (WAS) through magnetic drums because of its ferrimagnetic properties, and then reused (Evoqua Water Technologies 2017). The remaining portion is disposed of with the WAS or continues in further solids handling and treatment processes at the facility before disposal.

Some facilities use anaerobic digestion (AD) to reduce the quantities of the WAS from their WWT processes before disposal. AD is a biological WWT process that uses microorganisms to break down organic matter and produce biogas in the absence of oxygen. The biogas produced can be collected and used to offset energy costs at the facility. Biogas contains 50%-75% methane (CH₄), 25%-50% carbon dioxide (CO₂), and 2%-8% nitrogen (N₂), but may contain small amounts of hydrogen sulfide (H₂S) and other gases (Li et al. 2019). The energy content of biogas comes from CH₄. Therefore, before biogas is distributed in natural gas pipelines to consumers for use, it is cleaned to remove the CO₂, H₂S, moisture, and other impurities to a composition of about 95% CH₄, using processes such as absorption, adsorption, the use of membranes and so forth (Saber and Takach 2009).

CO₂ in the biogas is produced from the breakdown of organic matter during anaerobic fermentation as well as during methanogenesis (Metcalf and Eddy 2003). It is
not toxic to humans unless there is not enough air or oxygen present in the surrounding atmosphere. CO₂ does not contribute to the energy value in biogas; hence it is removed to purify the gas. H₂S gas is produced if the substrate that is fed to the digester contains some sulfur compounds such as sulfates, sulfites, or thiosulfates (Metcalf and Eddy 2003). H₂S gas is toxic to humans above permissible exposure limits (PELs), with a concentration of 100 ppm deemed immediately dangerous to life and health (IDLH) (OSHA 2020). H₂S is also highly flammable and corrosive to metal, and therefore undesirable in a biogas, because it may corrode metal pipes during transport and distribution of the gas. It also can damage concrete and other metal equipment and controls that are used in wastewater collection and treatment systems, such as sewers, pumps, and tanks (USEPA 1991). H₂S in anaerobic digesters (ADRs), sewers or biogas can be controlled by methods such as the use of air or oxygen to oxidize the sulfide (USEPA 1991; Saber and Takach 2009; Zafar 2020), the use of scrubbers to clean the gas (Saber and Takach 2009), raising the pH to inactivate the sulfate reducing bacteria (SRB) (USEPA 1991; Saber and Takach 2009), and addition of iron salts (USEPA 1991; Saber and Takach 2009; Zafar 2020), or iron oxides (Saber and Takach 2009; Zafar 2020) to precipitate the sulfide.

This study investigated the effect of adding Fe₃O₄, an iron oxide mineral, to the AD process on biogas production and composition (mainly CH₄ and CO₂), and on H₂S reduction and dissolved effluent iron concentration. Some of the studies that have examined the effect of Fe₃O₄ particles on CH₄ production during AD are summarized in Table 3.1. Studies such as those by Viggi et al. (2014), Lei et al. (2018), Jin et al. (2019), Liu et al. (2019), Cheng et al. (2020) and Aguilar-Moreno et al. (2020) found an increase
in the methane production rate. Wang et al. (2017), Lei et al. (2018), Aguilar-Moreno et al. (2020), Ajayi-Banji and Rahman (2021), Cheng et al. (2020) and Zhang et al. (2020) reported an increase in methane production, composition, or yield. Baek et al. (2016, 2017) also found an improvement in methanogenesis. Suanon et al. (2016) found an increase in the CH$_4$ volume at 0.5% Fe$_3$O$_4$ dose, but a decrease at 1.0% dose. The mechanism of increased CH$_4$ production in these studies was attributed to direct interspecies electron transfer (DIET) between exoelectrogenic microbes and methanogens facilitated by the addition of conductive materials (Fe$_3$O$_4$, in this case) to boost electric syntrophy between the two sets of microbes.

On the other hand, Zhao et al. (2018) found a negative effect on CH$_4$ production, in both the acetoclastic and hydrogenotrophic methanogenesis, which was explained by Fe$_3$O$_4$ competing for electrons with methanogens thereby hindering methanogenesis. However, hydrolysis and acidification were seen to increase via dissimilatory iron reduction, and an increase in CO$_2$ and acetate were observed. Jung et al. (2020) also did not observe a significant increase in methanogenesis. Andriamanohiarisoamanana et al. (2018) did not observe a significant effect on CH$_4$ yield with waste iron powder which was composed of 85% Fe$_3$O$_4$. Al-Essa et al. (2020) investigated the effect of different size Fe$_3$O$_4$ particles [small (50-150 nm), medium (168-490 nm) and large (800 nm-4.5 µm)] using fresh and degassed sludge and saw an increase in the CH$_4$ production rate with the fresh sludge for all particle sizes, but no difference in the total CH$_4$. With the degassed sludge, there was an increase in the CH$_4$ production rate with the medium-sized particles but little effect with the small and large particles, which decreased the cumulative CH$_4$. 
Table 3.1. Effect of Fe₃O₄ on methane production in anaerobic digestion

<table>
<thead>
<tr>
<th>Reference</th>
<th>Fe₃O₄ particle size</th>
<th>Fe₃O₄ dose</th>
<th>Application</th>
<th>Temp. (°C)</th>
<th>pH</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jin et al. (2019)</td>
<td>S1.2 µm</td>
<td>20 mM Fe</td>
<td>UASB</td>
<td>37</td>
<td>8.2</td>
<td>- 3-10 times increase in CH₄ production rate</td>
</tr>
<tr>
<td>Viggi et al. (2014)</td>
<td>S100-150 nm</td>
<td>0.35 g Fe/L</td>
<td>Batch</td>
<td>20-25</td>
<td>7.5-7.8</td>
<td>- 33% increase in CH₄ production rate from propionate degradation</td>
</tr>
<tr>
<td>Liu et al. (2019)</td>
<td>NA</td>
<td>10 g/L</td>
<td>SBRs</td>
<td>35</td>
<td>NA</td>
<td>- 21.7% increase in CH₄ production rate in reactor without sulfate with faster acetate and propionate degradation</td>
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<td></td>
<td></td>
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<td></td>
<td>- Improvement in methanogenesis in reactors with sulfate</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>- Increase in CH₄ production rates and CH₄ content</td>
</tr>
<tr>
<td>Lei et al. (2018)</td>
<td>S100</td>
<td>20 mM Fe</td>
<td>UASB</td>
<td>35</td>
<td>8.1</td>
<td>- Decrease in heavy metal concentration, ammonia nitrogen and calcium</td>
</tr>
<tr>
<td>Cheng et al. (2020)</td>
<td>C20 nm</td>
<td>200 mg/L</td>
<td>2-step batch</td>
<td>37</td>
<td>6.0 (1st stage)</td>
<td>8.0 (2nd stage)</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td>- 26.4% increase in CH₄ production rate in 2nd stage</td>
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<td></td>
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<td>- 22.9% increase in CH₄ yield</td>
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<td></td>
<td>- 73.9% increase in CH₄ yield</td>
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<td></td>
<td>- 55.5% increase in CH₄ production rate</td>
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<td></td>
<td></td>
<td>- &lt;10% increase in CH₄ yield</td>
</tr>
<tr>
<td>Aguilar-Moreno et al. (2020)</td>
<td>S4.2 nm</td>
<td>20 mg/L</td>
<td>Batch</td>
<td>36</td>
<td>7.7</td>
<td>- Increase in CH₄ volume at 0.5% dose, decrease in volume at 1% dose</td>
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<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>- Improvement in methanogenesis</td>
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<td></td>
<td>- 72.1% increase in CH₄ production</td>
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<td></td>
<td></td>
<td>- 27% reduction in acetoclastic methanogenesis, 22% reduction in hydrogenotrophic methanogenesis,</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- Increase in hydrolysis and acidification, increase in CO₂ and acetate</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- No significant increase in CH₄ production rate or yield</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- No significant increase in methane yield</td>
</tr>
<tr>
<td>Suanon et al. (2014)</td>
<td>S20 nm</td>
<td>0.5%, 1.0%</td>
<td>Batch</td>
<td>37</td>
<td>6.8-7.8</td>
<td>- Increase in H₂ in 1st stage</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>- 6.0% decrease in H₂ in 2nd stage</td>
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<td></td>
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<td></td>
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<td></td>
<td></td>
<td>- 72.4% increase in CH₄ production</td>
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<td></td>
<td></td>
<td>- 27% reduction in acetoclastic methanogenesis, 22% reduction in hydrogenotrophic methanogenesis,</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td>- Increase in hydrolysis and acidification, increase in CO₂ and acetate</td>
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<td></td>
<td></td>
<td></td>
<td>- No significant increase in CH₄ production rate or yield</td>
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<td></td>
<td></td>
<td></td>
<td>- No significant increase in methane yield</td>
</tr>
<tr>
<td>Back et al. (2016, 2017)</td>
<td>S100-700 nm</td>
<td>20 mM Fe</td>
<td>CSTR</td>
<td>35</td>
<td>7.0</td>
<td>- Increase in CH₄ production</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- Improvement in methanogenesis</td>
</tr>
<tr>
<td>Wang et al. (2017)</td>
<td>S0.5 - 1.0 mm</td>
<td>3g</td>
<td>Batch</td>
<td>35</td>
<td>7.0-7.1</td>
<td>- 72.4% increase in CH₄ production</td>
</tr>
<tr>
<td>Zhao et al. (2018)</td>
<td>S0.2 mm</td>
<td>10 g/L</td>
<td>Batch</td>
<td>37</td>
<td>7.14</td>
<td>- 27% reduction in acetoclastic methanogenesis, 22% reduction in hydrogenotrophic methanogenesis,</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>- Increase in hydrolysis and acidification, increase in CO₂ and acetate</td>
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<td></td>
<td></td>
<td></td>
<td>- No significant increase in CH₄ production rate or yield</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- No significant increase in methane yield</td>
</tr>
<tr>
<td>Jung et al. (2020)</td>
<td>S100-700 nm</td>
<td>2-20 mM Fe</td>
<td>CSTR</td>
<td>35</td>
<td>7.0</td>
<td>- Up to 32% increase in CH₄ production rate with all size particles but no difference in total CH₄, with the fresh sludge</td>
</tr>
<tr>
<td>Andriamanohiarisoamanana et al. (2018)</td>
<td>&lt; 20 µm (waste iron powder with 85% Fe₃O₄)</td>
<td>1-20 g/L</td>
<td>Batch &amp; semi-continuous</td>
<td>38</td>
<td>7.2-8.3</td>
<td>- For the degassed sludge, 12% increase in CH₄ production rate with the 168-490 nm particles, while the other size particles had little effect on CH₄ production rate but decreased cumulative CH₄</td>
</tr>
<tr>
<td>Al-Essa et al. (2020)</td>
<td>S50-150 nm, S168-490 nm, S800 nm - 4.5 µm</td>
<td>7 mM</td>
<td>Batch</td>
<td>36</td>
<td>~7.0</td>
<td>- Up to 32% increase in CH₄ production rate with all size particles but no difference in total CH₄, with the fresh sludge</td>
</tr>
</tbody>
</table>

Note: UASB = upflow anaerobic sludge blanket reactor; SBR = sequencing batch reactor; CSTR = continuously stirred tank reactor; SSAB = solid-state anaerobic batch reactor; C = commercial magnetite; S = synthesized magnetite; N = natural magnetite; and MNP = magnetite nanoparticles.
Other conductive materials that have been used to promote DIET for improved methanogenesis include hematite (Zhang et al. 2016), stainless steel (Li et al. 2017), activated carbon (Liu et al. 2012a), biochar (Chen et al. 2014; Zhao et al. 2016), zero valent iron (Liu et al. 2012b; Feng et al. 2014; Wu et al. 2015; Suanon et al. 2016; Wei et al. 2018; Zhao et al. 2018), and scrap iron (Zhang et al. 2014), among others.

Some of the studies that have investigated the effect of Fe$_3$O$_4$ on hydrogen sulfide and sulfate reduction in AD are summarized in Table 3.2. Jin et al. (2019) found a reduction in sulfate in solution which was attributed to DIET between iron (III)/SRB and methanogens. However, they reported that no iron sulfide (FeS) was found and that the H$_2$S in solution in the reactor with Fe$_3$O$_4$ was greater than that in the control reactor without Fe$_3$O$_4$. This could lead to an increase in H$_2$S in the gas phase unless another mechanism can be explained to prevent this. The H$_2$S in the gas phase was not analyzed. Jung et al. (2020) reported a decrease in the H$_2$S production rate and hence in the H$_2$S in the gas phase. The reduction in H$_2$S was attributed to sulfur formation due to DIET between exoelectrogenic anaerobic sulfide oxidizing bacteria and electrotrophic methanogens. Andriamanohiarisoamanana et al. (2018) also found a decrease in H$_2$S concentration in the gas phase using waste iron powder comprising 85% Fe$_3$O$_4$. The reduction in H$_2$S was assumed to be a result of FeS precipitation due to a black precipitate that was observed. However, because the iron waste was not composed of pure Fe$_3$O$_4$, it cannot be determined if the results were due to the Fe$_3$O$_4$ fraction, the remaining fraction of the waste iron powder, or both. Ajayi-Banji and Rahman (2021) found an increase in the H$_2$S gas. Zhang et al. (2016) investigated the effect of Fe$_3$O$_4$ on
the reduction of dissolved H$_2$S in sewage at 20°C and found a decrease in sulfide formation. However, this temperature is not common in ADRs.

Due to some conflict in the results of previous studies, this research investigated whether Fe$_3$O$_4$ with the specifications used in the BioMag® process for WWT could have an effect on the AD process in terms of biogas production (mainly CH$_4$), biogas composition [because studies such as Zhao et al. (2018) reported a decline in methanogenesis and an increase in CO$_2$], and a reduction in the H$_2$S concentration in the biogas to less than 100 ppm, which is IDLH (OSHA 2020), for those WWT facilities that use the BioMag® technology and proceed with AD for sludge stabilization. Because this study used the same Fe$_3$O$_4$ as that supplied for the BioMag® process, it is expected that the results are similar to what would be observed at facilities using this technology. As discussed previously, Al-Essa et al. (2020) observed some differences in results when different sizes of the Fe$_3$O$_4$ particles were used. The particle size of the Fe$_3$O$_4$ is emphasized because smaller particles, such as in the nanometer size range, may act differently, especially because they have a higher surface area to volume ratio which may increase their adsorption properties, thus adding another dimension to the treatment processes occurring within the ADR. For example, Lei et al. (2018) observed a decrease in heavy metal concentration in anaerobic reactors amended with Fe$_3$O$_4$ nanoparticles.

This research also investigated the transformation of Fe$_3$O$_4$ into dissolved iron (Fe), and whether this could have implications on the AD products, and effluent quality in terms of dissolved iron concentration leaving the system, especially because Fe$_3$O$_4$ is said to be insoluble in water (Perry et al. 1997; Evoqua Water Technologies 2017).
Table 3.2. Effect of Fe$_3$O$_4$ on sulfate reduction and H$_2$S production in anaerobic digestion

<table>
<thead>
<tr>
<th>Reference</th>
<th>Fe$_3$O$_4$ particle size</th>
<th>Fe$_3$O$_4$ feed</th>
<th>Applicat...</th>
<th>Temp. (°C)</th>
<th>pH</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jin et al. (2019)</td>
<td>$^{s}$1.2 µm</td>
<td>20 mM Fe</td>
<td>UASB</td>
<td>37</td>
<td>8.2</td>
<td>- Decreased sulfate; increased H$_2$S in solution</td>
</tr>
<tr>
<td>Jung et al. (2020)</td>
<td>100 - 700 nm</td>
<td>8+ mM Fe</td>
<td>CSTR</td>
<td>35</td>
<td>7.0</td>
<td>- Decreased H$_2$S production rate</td>
</tr>
<tr>
<td>Andriamanohiarisoamanana et al. (2018)</td>
<td>&lt; 20 µm (waste iron powder with 85% Fe$_3$O$_4$)</td>
<td>1-20 g/L Fe</td>
<td>Batch &amp; semi-continuous</td>
<td>38</td>
<td>7.6-7.8</td>
<td>- 93-99% decrease in H$_2$S in the gas phase</td>
</tr>
<tr>
<td>Zhang et al. (2016)</td>
<td>45 - 60 µm</td>
<td>40 mg/L</td>
<td>Batch</td>
<td>20</td>
<td>~6.5-7.3</td>
<td>- 79% decrease in dissolved H$_2$S in sewage</td>
</tr>
<tr>
<td>Ajayi-Banji and Rahman (2021)</td>
<td>$^{c}$15-20 nm</td>
<td>20 mg/L</td>
<td>SSAB</td>
<td>35</td>
<td>6.7-9.5</td>
<td>- Two-fold increase in H$_2$S gas</td>
</tr>
</tbody>
</table>

Note: UASB = upflow anaerobic sludge blanket reactor; CSTR = continuously stirred tank reactor; SSAB = solid-state anaerobic batch reactor; $^c$ = commercial magnetite; $^s$ = synthesized magnetite.
Previous studies that used Fe\textsubscript{3}O\textsubscript{4} in AD did not consider the potential impact of an increase in the effluent iron content beyond the AD process due to Fe\textsubscript{3}O\textsubscript{4} addition. High concentrations of iron in water can be a problem and may require additional treatment methods to remove the iron from the effluent (IDPH 2010), which would come at an additional cost. The USEPA secondary maximum contaminant level (SMCL) for iron in drinking water is 0.3 mg/L (USEPA 2021); above this level, iron can leave reddish-brown stains and deposits on utensils, plumbing, laundry, and so forth (IDPH 2010). High iron concentration in drinking water also can produce an undesirable taste or color in food (IDPH 2010; APHA 2017) and can attract iron bacteria which can cause odors and leave a residue that can clog plumbing (IDPH 2010). According to the World Health Organization (WHO 2003), iron is lethal at doses of 200-250 mg/kg of body weight, although death has occurred at doses around 40 mg/kg. For irrigation water, the United Nations Food and Agricultural Organization (UNFAO) recommends a limit of 5 mg/L Fe (APHA 2017). This study also examined the digester for any bottlenecks which could be caused by the heavy Fe\textsubscript{3}O\textsubscript{4} particles and could hinder the AD process, in terms of mixing of the digester contents and other impacts.

The origin of this study was the Marlay-Taylor Water Reclamation Facility (Lexington Park, Maryland) which uses Fe\textsubscript{3}O\textsubscript{4} in its WWT process and digests its WAS anaerobically. It was noted that at this facility, the percent volatile solids (VS) destruction in the ADRs increased since the facility began using Fe\textsubscript{3}O\textsubscript{4}. However, no data were available to compare the biogas production and composition between the pre- and post-Fe\textsubscript{3}O\textsubscript{4}-use periods, and to determine if the effect was due to the Fe\textsubscript{3}O\textsubscript{4}. This research therefore investigated whether Fe\textsubscript{3}O\textsubscript{4} could have additional benefits beyond its use in the
BioMag® process in secondary WWT, specifically in the AD process, and to recommend recovery and recycling of the Fe₃O₄ back to the bioreactors at the WWT facility after the AD process, instead of after sedimentation and before AD, if additional benefits were found. AD reduces the sludge quantities to be wasted and therefore the amount of sludge to be processed to recover the Fe₃O₄ would decrease significantly, reducing the load on the recovery equipment, time, and cost of recovery.

3.2 Materials and Methods

3.2.1 Anaerobic Digester Setup

The digester setup is shown in Fig. 3.1. It comprised a 10-L glass anaerobic reactor tank (the digester) with an active volume of 3.4 L, a feeding and sampling point, a pump to aid in mixing of the digester contents by continuous circulation, an insulated heating jacket wrapped around the digester to heat its contents, a temperature controller with the desired temperature set at 35°C, a thermocouple to measure the temperature inside the digester, a gas collection system made of two plastic cylindrical containers that used the fluid displacement method, a gas release and sampling point, and Tygon® tubing (Saint-Gobain Performance Plastics, Akron, Ohio) to aid in circulating the digester contents and to transport the produced gas to the gas collection system. The displacement fluid in the gas collection system was a mixture of 4 g/L sodium chloride in 5% sulfuric acid solution to limit CO₂ absorption and microbial growth within the fluid, and a few drops of methyl red for color, to make it easy to determine the level of the fluid (Kesaano 2011; Ahmadi and Dupont 2018). The temperature of the digester was maintained within the mesophilic temperature range.
3.2.2 Feeding and Sampling

Whey protein was used as the substrate for the AD process, in the form of a sweet whey powder. Whey is one of the two main proteins found in milk and constitutes about 20% of the total milk protein; the other protein is casein, which constitutes about 80% of the total milk protein (Qi and Onwulata 2011; Gunnars 2018). Whey is found in the liquid portion of milk, which is separated during the process of making cheese (Qi and Onwulata 2011; Gunnars 2018) and has a considerable amount of sulfur amino acids (Freeman 2005; Baldwin et al. 2020). Therefore, it is expected that the AD of sweet whey would produce some H$_2$S gas, in addition to the biogas.

Before feeding the digester, a known volume (600 mL) of the digestate was sampled out and then the same volume of deionized water was added to the digester along with the feed. 2.8 g whey protein was fed to the digester every 2-3 days along with
0.5-0.55 g calcium hydroxide [Ca(OH)$_2$] powder. The role of Ca(OH)$_2$ was to add alkalinity to maintain the pH within the desired range, due to the high concentration of CO$_2$ gas produced in anaerobic reactors, which could easily decrease the pH and affect CH$_4$ production, because the CH$_4$-producing bacteria are sensitive to small pH changes (Metcalf and Eddy 2003; Schnaars 2012). The optimal pH for AD lies in the range 6.5-7.6 (McCarty 1964; Riffat 2013).

The particle size of the Fe$_3$O$_4$ powder was 10-15 µm (Evoqua Water Technologies 2020), and the ratio of Fe$_3$O$_4$ to whey protein added was 1:1, by weight. This ratio was chosen because the BioMag® process is designed with a 1:1 ratio of Fe$_3$O$_4$ to suspended solids (Evoqua Water Technologies 2017), and this study would like to recommend that the Fe$_3$O$_4$ be recovered from the WAS after AD instead of before, for those facilities that digest their sludge anaerobically before disposal. Ferrous chloride (FeCl$_2$) also was added to the digester at the same ratio to compare the effect of Fe$_3$O$_4$ with that of FeCl$_2$ which is more soluble.

The experimental period was divided into the Pre_Fe$_3$O$_4$ period before the introduction of Fe$_3$O$_4$ to the digester, the Add_Fe$_3$O$_4$ period when Fe$_3$O$_4$ was added, the Halt_Fe$_3$O$_4$ period when Fe$_3$O$_4$ feeding was discontinued, the Add_Fe$^{2+}$ period when FeCl$_2$ was added, and the Halt_Fe$^{2+}$ when FeCl$_2$ addition was discontinued.

3.2.3 Iron Analysis

Iron analysis was performed to establish whether there was any dissolution of the Fe$_3$O$_4$ in the anaerobic digester and determine the effluent iron concentration, and if there was a relationship between the dissolved iron and concentration of H$_2$S gas in the digester, as well as with the gas volume and composition. The samples for iron analysis
were collected in an amber bottle to minimize exposure to light, and the bottle was filled to the brim and immediately capped to minimize exposure to air, as Fe\(^{2+}\) will easily oxidize to Fe\(^{3+}\) (APHA 2017). The samples then were filtered through a 0.45-µm filter to analyze for dissolved iron (USEPA 1983; Metcalf and Eddy 2003).

Iron was measured using a Hach DR 3900 spectrophotometer, (Hach, Loveland, Colorado), following the 1,10-phenanthroline method for ferrous iron (Hach 2019) and the USEPA FerroVer method for total iron (Hach 2014) using powder pillows, with a measurement range of 0.02-3.00 mg/L for both methods (Hach 2014, 2019). When the results were above the measurement range, the samples were diluted before measurement and the actual concentration of the samples calculated. On every sampling or feeding day, analysis for soluble iron was conducted in triplicate, or sometimes in duplicate, and the average taken.

To verify the accuracy of the Fe\(^{2+}\) measurements, the standard solution method in the Hach test procedure was followed. For the first few samples that were prepared, the readings were much lower than the expected results for the standard, were unstable, and were not within the 95% confidence interval suggested in the procedure. The pH of these samples was between 5 and 6. However, when the pH of the standard solution was decreased to between 2.5 and 4 using 6N hydrochloric acid (HCl), the readings were within acceptable limits and were stable. Therefore, the pH of all subsequent samples was dropped to within this range before measurement. The standard additions method in the Hach test procedure was used to check the accuracy of the total iron test, and it was determined that there were no interferences in the measurements and the results were within acceptable limits.
Because Fe$^{2+}$ easily could oxidize to Fe$^{3+}$ after the digestate was out of the reactor, and because the digestate samples were vacuum-filtered before analysis, which could affect the proportions of Fe$^{2+}$ and Fe$^{3+}$ in the samples, only the results for the total dissolved iron are reported, because these could be measured more accurately. The total dissolved iron concentration (Fe) in the digestate was measured over time to establish the background Fe before adding Fe$_3$O$_4$. This concentration was compared to the Fe after adding Fe$_3$O$_4$ to the reactor to determine if there was transformation of the Fe$_3$O$_4$ into dissolved iron.

3.2.4 Solubility of Magnetite

A series of tests were carried out to determine whether the Fe$_3$O$_4$ powder would dissolve in water. Fe was measured. These tests were conducted at room temperature and under open-air conditions in the laboratory. The factors considered were contact time (with deionized water), Fe$_3$O$_4$ dose, and mixing speed.

To determine the effect of contact time on Fe$_3$O$_4$ solubility, 1 g Fe$_3$O$_4$ was added to 100 mL deionized water and immediately stirred at 200 revolutions per minute (rpm) for 5, 25, 45 and 65 min, after which the Fe$_3$O$_4$ was immediately filtered from the mixture. The pH of all filtered samples was reduced to between 3 and 4 using 6N HCl before measuring Fe. This test was done in triplicate.

The effect of Fe$_3$O$_4$ dose on Fe$_3$O$_4$ solubility was determined by adding 1, 2, 3, 4, 7 and 10 g Fe$_3$O$_4$ powder to 100 mL deionized water and stirring at 200 rpm for 20 min, after which the Fe$_3$O$_4$ immediately was filtered out, the pH was adjusted, and the Fe was measured.
The effect of mixing speed was determined by adding 1 g Fe₃O₄ powder to 100 mL deionized water and stirring for 20 min at 200, 400, 600 and 800 rpm. The samples immediately were filtered, the pH was adjusted, and Fe was measured. This test was duplicated.

3.2.5 H₂S Analysis

The analysis of H₂S in the digester gas involved measurement of the H₂S concentration using an HT-1805 four-in-one gas detector (High Tech Instruments, Dongguan, Guangdong, China) in parts per million (ppm). To obtain the actual concentration of H₂S in the digester gas, a calibration curve was created. This was done by preparing known concentrations of H₂S from 100-ppm H₂S calibration gas by diluting known volumes of the calibration gas with known volumes of air. The calibration curve was then developed by plotting the known concentration of the prepared gases against their reading from the detector. The concentration of H₂S in the digester gas was obtained each time by taking a detector reading in triplicate, averaging it, and then using the calibration curve to determine the actual concentration in the digester gas.

3.2.6 Gas Volume Measurement

The volume of gas produced was determined using the fluid displacement method. The height of the displaced fluid in the gas collection tank was measured before sampling out the digestate and feeding. Because the gas collection tank was cylindrical, the gas volume in milliliters (mL) was calculated from, \( V = \pi r^2 h \times 0.001 \), where \( r \) is the radius of the tank in millimeters, \( h \) is the height of displaced fluid in millimeters and 0.001 is a conversion factor from cubic millimeters to milliliters.
3.2.7 Gas Composition Analysis

The composition of the digester gas was analyzed using a GOW-MAC series 400 G/C (GOW-MAC Instrument, Bethlehem, Pennsylvania) gas chromatograph (GC), with a thermal conductivity detector. The GC used helium as the carrier gas. The detector, column and injector temperature were set at 110, 100 and 72°C, and the detector current was set at 100 mA. A 5-mL sample of the digester gas was collected using a glass syringe and injected into the GC for analysis. The gas was analyzed for CH₄, CO₂, N₂ and O₂, and the percentage of each gas in the mixture was determined. Calibration for CH₄ and CO₂ was done with 100% CH₄ and 100% CO₂, respectively, while calibration for oxygen and nitrogen was done with ambient air, which consists of about 78% N₂ and 20.5% O₂. The gas composition was compared to ascertain if there were any significant changes before and after the addition of Fe₃O₄ and FeCl₂ to the digester.

3.2.8 Statistical Analysis

R programming, using R Studio version 1.3.1093, was used to analyze the data obtained from the laboratory, using a method called intervention analysis, which was described by Berthouex and Brown (1994, 2002), Booman et al. (1986), Pallesen et al. (1985) and Box and Tiao (1975). This method can be used to analyze data with a serial correlation (Box and Tiao 1965; Berthouex and Brown 2002). The method is used to predict time series, and the approach discussed by Ayaa et al. (2020) was used, in which the time series before and after the intervention are forecast forward. This method was used because the maximum effects of the interventions, which in this study were defined by adding Fe₃O₄, halting Fe₃O₄ addition, adding FeCl₂, and halting FeCl₂ addition, were expected to be realized at the end of each intervention period.
3.3 Results and Discussion

3.3.1 Magnetite Solubility

The effects of contact time of the Fe$_3$O$_4$ with deionized water, Fe$_3$O$_4$ dose, and mixing speed are shown in Fig. 3.2. Fe represents the dissolved Fe$_3$O$_4$ iron. The solubility of the Fe$_3$O$_4$ powder increased with an increase in contact time with deionized water [Fig. 3.2(a)]. Three independent tests were carried out and they produced similar results with trendlines that were parallel and in close proximity to each other. The solubility of the Fe$_3$O$_4$ decreased with increase in Fe$_3$O$_4$ dose [Fig. 3.2(b)]. This could be because the Fe$_3$O$_4$ accumulated on the magnetic stirrer bars due to its ferrimagnetism, clumping together and thus decreasing the contact surface with the water, or it could be due to a simple “salting out” effect due to increases in dissolved ion concentrations. The solubility of the Fe$_3$O$_4$ increased with increase in mixing speed [Fig. 3.2(c)], which suggests that the elimination of local concentration gradients increases Fe$_3$O$_4$ solubility. This test was conducted in duplicate, and hence there are two trendlines.

Fig. 3.2 shows, therefore, that some of the Fe$_3$O$_4$ dissolved in water at room temperature and under open air conditions. Fig. 3.3 shows the color change in the water after stirring for 20 mins at doses of 2, 3 and 4 g Fe$_3$O$_4$, and some of the dark brown residue left on the filters after filtering the colored solutions. The next step was to determine if the Fe$_3$O$_4$ dissolved under anaerobic conditions, and if so, whether this might affect the biogas production and composition, and H$_2$S concentration in the digester gas.
3.3.2 **H₂S Production**

The effect of Fe₃O₄ on H₂S in the digester gas is shown in Fig. 3.4(a). In the Pre_Fe₃O₄ period (Days 1-5), the Fe and H₂S levels were consistent, averaging about 138
ppm H$_2$S and 0.03 mg/L Fe. These were the background concentrations, before Fe$_3$O$_4$ addition. As Fe$_3$O$_4$ was added, from Day 6 to 15 (the Add_Fe$_3$O$_4$ period), the Fe began to increase, but the H$_2$S remained constant until the Fe was about 1.30 mg/L. At this point, the H$_2$S decreased by about 23 ppm (17%) to a concentration of 115 ppm. The H$_2$S continued to decrease with Fe$_3$O$_4$ addition to 79 ppm, a 43% decrease at the end of the Add_Fe$_3$O$_4$ period, with the Fe equal to 1.38 mg/L at this point. Hence this period indicates a general decrease in H$_2$S with increase in Fe. From Day 16 to 22 (the Halt_Fe$_3$O$_4$ period), Fe$_3$O$_4$ addition had been discontinued, although most of the Fe$_3$O$_4$ previously added continued to circulate in the digester with the sludge. During this period, both the Fe and H$_2$S initially decreased on Day 16 to 1.16 ppm Fe and 70 ppm H$_2$S, indicating a 49% decrease in H$_2$S from the initial concentration of 138 ppm. However, the Fe increased from this day to Day 18, whereas the H$_2$S remained at about 71 ppm. From Day 18 to 20, the H$_2$S increased further with decreasing Fe, whereas from Day 20 to 22, the H$_2$S decreased with increasing Fe. The dissolved iron concentration during this period was odd, increasing and decreasing, but the corresponding behavior of H$_2$S appeared consistent, with a decrease in H$_2$S with increase in Fe and vice versa.

The behavior of the Fe$^{2+}$-Fe$^{3+}$ redox couple within the anaerobic digester environment raises a number of interesting questions that merit further study. While ferric (+3) iron must be reduced to ferrous (+2) in order to detect an increase in iron solubility, it is unclear how ferrous iron would become reoxidized in a strong reducing environment leading to reduced iron solubility. One possibility is that iron may play a role in the temporary “storage” of chemical reducing power. In other words, ferrous (+2) iron may temporarily retain its reducing power (electrons) until it interacts with another
chemical and/or biological agent to which it can rapidly transfer those electrons and return to its fully oxidized (i.e., ferric) state.

Fe$_3$O$_4$ addition was stopped after Day 16 due to clogging problems, which may be attributed to the accumulation of Fe$_3$O$_4$ and thickening of the sludge making it more difficult to pump through the Tygon® tubing circulating the digester contents. Clogging will lead to inadequate mixing of the digester contents, which could contribute to the
inconsistent behavior of the Fe seen in the Halt_Fe$_3$O$_4$ period. Adequate mixing is crucial for optimum performance of the digester (Metcalf and Eddy 2003; Riffat 2013). The increase in Fe during this period could be explained by an increase in the dissolved Fe$_3$O$_4$ due to longer residence time of the Fe$_3$O$_4$ in the digester and/or a reduced opportunity for ferrous (+2) iron to transfer its reducing power to another chemical species enabling it to reoxidize to ferric (+3) iron. This effect is also shown in Fig. 3.2(a) where the solubility of Fe$_3$O$_4$ increased with increase in contact time. The pH from the start of the Pre_Fe$_3$O$_4$ period to the end of the Halt_Fe$_3$O$_4$ period ranged from 6.5 to 6.7, with an average of 6.6, which was within the pH range mentioned previously that is suitable for AD. The AD temperature was mesophilic, ranging from 33°C to 38°C with an average of 36°C.

To investigate whether the dissolved Fe$_3$O$_4$ iron could be a cause of the reduction in H$_2$S, a more soluble iron compound (FeCl$_2$) was added to the digester during feeding. The effect of this can be seen on Days 23-30 in Fig. 3.4(b). FeCl$_2$ was added on Day 22 and Day 23, and the effect of this can be seen on Days 23 and 24. On Day 22, before FeCl$_2$ was added, the Fe was 1.7 mg/L and H$_2$S was 85 ppm. After adding 2.8 g FeCl$_2$, the Fe rose to 85 mg/L, whereas the H$_2$S decreased to 27 ppm: a reduction in H$_2$S of about 68% from the previous sampling day. Another 2.8 g FeCl$_2$ was added on the next sampling day, doubling the Fe to about 170 mg/L and decreasing the H$_2$S further to 10 ppm. During the next two sampling days, FeCl$_2$ addition was discontinued (the first Halt_Fe$^{2+}$ period) and the Fe decreased. This occurred on Days 25 and 26. At this point, a decision was made to add more FeCl$_2$ until the H$_2$S concentration decreased to 0. This occurred on days 27-30 in the second Add_Fe$^{2+}$ period. The Fe increased to about 400
mg/L, and at this point, the H₂S had been purged from the system. This occurred on Day 30.

FeCl₂ addition was discontinued on Day 30. From this day onward (the second Halt_Fe²⁺ period), the Fe began to decrease. A general trend occurred of the H₂S increasing again as the Fe decreased. Some of the large fluctuations in H₂S are believed to be a result of ferrous (+2) iron reoxidizing to ferric (+3) iron through transient electron transfer resulting in the removal of soluble ferrous iron from the AD environment. Although at this point this theory is speculation, a number of studies suggest that transient electron transfer through the ferric-ferrous redox couple can result in the reduction of water to produce hydrogen. USEPA (1991), Saber and Takach (2009) and Zafar (2020) mention the addition of air or oxygen as one of the methods that can be used to remove H₂S from biogas through oxidation, and from observation, the inadvertent introduction of oxygen into the AD during feeding seemed like another possible cause of the fluctuations in H₂S seen during this period.

Feeding continued beyond Day 30 in an effort to determine the length of time required to return the digester to pre-Fe₃O₄ conditions. This process proved to be uneconomical because only about 50% of the H₂S had been recovered between Days 30 and 89. At Day 89, the Fe and H₂S were 4.46 mg/L and 78 ppm, respectively. The conclusion was that the effects of the iron were long-lasting, because the residence time of the Fe was long enough to slow the increase of the H₂S levels back to the original conditions before any iron was added to the digester. This observation supports the contention that the ferrous-ferric redox couple may play a significant role in mediating chemical reactions within the AD environment. For example, oxidized sulfur species as
well as other inorganic or organic chemical may be suitable chemical repositories for the reducing power of ferrous (+2) iron. It is possible that only after the concentrations of reduced iron species have been completely exhausted and ferric (+3) iron is the dominant iron species would H₂S concentrations return to pre-iron conditions. At 4.46 mg/L Fe, the effluent water can be used for irrigation, according to the UNFAO (the limit is 5 mg/L) (APHA 2017), and the H₂S at 78 ppm is not immediately dangerous to life and health, according to OSHA.

As discussed previously, the literature has suggested that the addition of conductive material to the AD process fosters direct interspecies electron transfer (DIET) enabling exoelectrogenic and electrotrophic microbes to exchange electrons directly, accelerating the AD process. Jung et al. (2020) attributed the reduction of H₂S gas in the digester to the anaerobic oxidation of sulfide to elemental sulfur via DIET between exoelectrogenic sulfur oxidizing bacteria and electrotrophic methanogens. Jung et al. (2020) did not observe any FeS in the digestate. Jin et al. (2019) did not analyze H₂S in the gas phase but found a reduction in the sulfate in solution and an increase in H₂S in solution, which could lead to an increase in H₂S in the gas phase when it escapes from solution. Jin et al. (2019) also did not observe FeS in the digestate. Andriamanohiarisoamanana et al. (2018) found a decrease in H₂S in the gas phase which they attributed to the formation of FeS. However, waste iron powder was used, which contained 85% Fe₃O₄; therefore, it is possible that the results seen could also be due to the remaining 15% fraction of the waste iron powder, and not (entirely) due to the Fe₃O₄.

The present study found a relationship between Fe and H₂S (Fig. 3.4). Therefore, it is possible that the reduction in the H₂S concentration in the gas was due to the
reduction of sulfite and/or sulfate by Fe, forming FeS. Or as previous literature suggests, it could be due to an enhancement of sulfide removal by Fe$_3$O$_4$-enabled DIET, but accompanied with FeS formation as suggested by Andriamanohiarisoamanana et al. (2018). With Fe$_3$O$_4$ addition, the digestate was a dark gray residue which may suggest iron sulfide (FeS) formation. However, it was difficult to distinguish the Fe$_3$O$_4$ from the residue. No yellow sulfur deposits were physically observed in the digestate; hence it could not be determined whether there was sulfur granule formation. When FeCl$_2$ was added to the digester, the digestate residue was the same dark grey color observed after Fe$_3$O$_4$ addition. Hence, it is suspected that the mechanism of H$_2$S reduction by Fe$_3$O$_4$ could be due to the precipitation of sulfide by the dissolved iron, but the possibility of sulfur formation as suggested by Jung et al. (2020) was not ruled out.

The Fe in the digester effluent reached 1.7 mg/L after Fe$_3$O$_4$ was added. Jin et al. (2019) found a dissolved iron concentration of 5.81 mg/L after an 80-day experiment feeding an upflow anaerobic sludge blanket (UASB) reactor with Fe$_3$O$_4$ at 20 mM Fe. The SMCL for iron in drinking water is 0.3 mg/L Fe; above this level, iron can cause a staining effect, plumbing problems, and other aesthetic issues (IDPH 2010). Above 0.3 mg/L, iron can plug micro irrigation equipment; above 1.0 mg/L, it can cause spotting in plant leaves, with overhead irrigation systems; and above 5.0 mg/L, it can cause toxicity in some plant species (Swistock 2016). The UNFAO recommends a limit of 5 mg/L Fe in irrigation water (APHA 2017). If high Fe effluent from ADRs is directed back to the WWT facility, it may lead to an accumulation of Fe in the reactors and may require additional methods of removal, which incur additional cost.
To quantify properly the effect of Fe on H$_2$S in the digester gas, intervention analysis was used (Table 3.3). The difference in Fe and H$_2$S between the Pre$_3$Fe$_2$O$_4$ and Add$_3$Fe$_2$O$_4$ periods, and between the Add$_3$Fe$_2$O$_4$ and Halt$_3$Fe$_2$O$_4$ periods, was determined by predicting the values at the end of these periods using intervention analysis, which uses the exponentially weighted moving average (EWMA) models [Figs. 3.4(c and d), for Fe and H$_2$S, respectively]. The corresponding model residuals are shown in Figs. 3.4(e and f). The estimated overall moving average parameter, $\theta$, for both Fe and H$_2$S, was zero, which indicates that these models approximated the white noise model, as explained by Berthouex and Brown (2002) and Pallesen et al. (1985). The estimated difference, $\delta$, in H$_2$S between the Pre$_3$Fe$_2$O$_4$ and Add$_3$Fe$_2$O$_4$ periods was $-59 \pm 8.2$ ppm, which was a 43% reduction in H$_2$S in the Add$_3$Fe$_2$O$_4$ period, whereas the difference in Fe was $1.35 \pm 0.06$ mg/L. The effect of the Fe$_3$O$_4$ is believed to have continued in the Halt$_3$Fe$_2$O$_4$ period, because a further reduction in H$_2$S occurred at about 70 ppm, implying a 49% reduction in H$_2$S at this point. The estimated difference in H$_2$S in the Halt$_3$Fe$_2$O$_4$ was $6 \pm 6.4$ ppm, while that of Fe was $0.29 \pm 0.48$ mg/L.

The model residuals for Fe in Fig. 3.4(e) seem to be random, indicating that the EWMA model was a good fit for the data. On the other hand, the model residuals for H$_2$S in Fig. 3.4(f) do not seem random in the Pre$_3$Fe$_2$O$_4$ period and half of the Add$_3$Fe$_2$O$_4$ period. This is because the H$_2$S values during this period were essentially the same, hence the residuals equaled zero.

3.3.3 Gas Production

Fig. 3.5(a) shows the effect of Fe$_3$O$_4$ on the gas volume, $V$, whereas Fig. 3.5(b) includes the effect of FeCl$_2$. No significant increase in $V$ occurred in the Add$_3$Fe$_2$O$_4$
period, whereas there was a slight decline in the Halt_\(\text{Fe}_3\text{O}_4\) period [Fig. 3.5(a)]. An increase in \(V\) occurred from Day 23 to day 32 [Fig. 3.5(b)], when there were higher Fe concentrations in the digester, which could be attributed to the corresponding lower concentrations of \(\text{H}_2\text{S}\) in this period [Fig. 3.4(b)].

![Graphs showing gas volume effects](image)

**Fig. 3.5.** (a) Effect of \(\text{Fe}_3\text{O}_4\) addition on gas volume; (b) effect of \(\text{FeCl}_2\) addition on gas volume; (c) EWMA model for gas volume; and (d) model residuals for the gas volume.

The effect of \(\text{Fe}_3\text{O}_4\) on the gas volume was estimated using intervention analysis. The results are presented in Fig. 3.5(c), which shows the EWMA model for \(V\), and in Fig. 3.5(d), which shows the model residuals. The model residuals seem random, implying that the model was a good fit for the data. The overall moving average parameter, \(\theta\), for the \(V\) time series from Fig. 3.5(a) was estimated to be 1. This indicates that the model approximated the random walk model described by Berthouex and Brown (2002) and Pallesen et al. (1985). The estimated difference, \(\delta\), between the Pre_\(\text{Fe}_3\text{O}_4\) and
Add $\text{Fe}_3\text{O}_4$ periods was $11 \pm 0$ mL, indicating a 0.8% increase in $V$ due to $\text{Fe}_3\text{O}_4$ addition. The results are given in Table 3.3.

Table 3.3. Results from statistical intervention data analysis

<table>
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<th>Parameter</th>
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<th>H$_2$S</th>
<th>V</th>
<th>CH$_4$</th>
<th>CO$_2$</th>
<th>N$_2$</th>
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</tr>
<tr>
<td>$\theta$</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
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<tr>
<td>Pre.pred.</td>
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<td>138</td>
<td>1378</td>
<td>68</td>
<td>25.76</td>
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<tr>
<td>Add.pred.</td>
<td>1.38</td>
<td>79</td>
<td>1389</td>
<td>66</td>
<td>26.81</td>
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<td>Halt.pred.</td>
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<td>1300</td>
<td>70</td>
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<td>$\delta_1$</td>
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<td>-2.0</td>
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<tr>
<td>$\delta_2$</td>
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<td>-89.0</td>
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<td>0</td>
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Note: $\theta$ is the estimated overall moving average parameter for the entire time series; Pre.$\theta$, Add.$\theta$ and Halt.$\theta$ are the estimated moving average parameters for the Pre-, Add- and Halt.$\text{Fe}_3\text{O}_4$ periods, respectively; Pre.pred., Add.pred. and Halt.pred. are the predicted values for the Pre-, Add- and Halt.$\text{Fe}_3\text{O}_4$ periods, respectively; $\delta_1$ and $\delta_2$ are the estimated differences between the Pre- and Add.$\text{Fe}_3\text{O}_4$ periods and the Add- and Halt.$\text{Fe}_3\text{O}_4$ periods, respectively; Stdev. are the standard deviations in the estimated values for $\delta_1$ and $\delta_2$.

3.3.4 Gas Composition

Fig. 3.6(a) shows the relationship between CH$_4$, CO$_2$, N$_2$ and O$_2$ in the digester gas and the Fe in the digester due to $\text{Fe}_3\text{O}_4$ addition, and Fig. 3.6(b) includes the effect due to the addition of FeCl$_2$. Generally, there were no significant changes in the CH$_4$, CO$_2$, N$_2$ and O$_2$ composition due to magnetite addition. However, a slight decrease in CH$_4$ corresponding to a slight increase in CO$_2$ occurred during Days 23-32 after FeCl$_2$ was added. Figs. 3.7(a), 3.8(a) and 3.9(a) show the effect of $\text{Fe}_3\text{O}_4$ on CH$_4$, CO$_2$ and N$_2$, respectively, and Figs. 3.7(b), 3.8(b) and 3.9(b) include the effect of FeCl$_2$. The intervention analysis results are shown in Figs. 3.7(c), 3.8(c) and 3.9(c) and Figs. 3.7(d),
3.8(d) and 3.9(d). A 2.0% ± 0% reduction in CH₄ occurred in the Add_Fe₃O₄ period and a 4.0% ± 0% increase occurred in the Halt_Fe₃O₄ period. For CO₂, a 1.1% ± 0.79% occurred in the Add_Fe₃O₄ period and a 2.7% ± 0.77% decrease occurred in the Halt_Fe₃O₄ period. A 1% increase in N₂ occurred in the Add_Fe₃O₄ period and a 1% reduction occurred in the Halt_Fe₃O₄ period. The results are summarized in Table 3.3.

The models for CH₄ and N₂ approximated the random walk model (θ = 1), whereas the model for CO₂ approximated the white noise-random walk model (θ = 0.2244), as described by Berthouex and Brown (2002) and Pallesen et al. (1985).

No defined relationship could be established between the gas percentages and the changes in Fe when Fe₃O₄ was added, and the estimated differences in Table 3.3 seem to be too small to conclude or establish any significant relationship between the two. The CH₄ composition in the Pre_Fe₃O₄ period ranged from 67% to 70% with an average of 69%, and in the Add_Fe₃O₄ period the range was 64%-70%, with an average of 67%. The CO₂ in the Pre_Fe₃O₄ period ranged from 24% to 26%, with an average of 25%, whereas in the Add_Fe₃O₄ period the range was 24%-27%, with an average of 26%. The average N₂ in both periods was 5%. Hence, it can be concluded that there were no significant changes in the gas composition due to Fe₃O₄ addition in the digester. The increase in V mentioned previously seemed to be due to an increase in CO₂ during days 23-32 [Fig. 3.6(b)]. CH₄ decreased during this period. The CO₂ during this period ranged from 28% to 29%, with an average of 29%, whereas the CH₄ ranged from 65% to 66%, with an average of 65%, indicating a slight decrease in CH₄ and a slight increase in CO₂. Hence there seemed to be an inhibitory effect on CH₄ production, possibly due to elevated iron levels during this period, which was due to the addition of FeCl₂.
Because the AD process, by definition, takes place in the absence of oxygen, it was important to determine the percentage of oxygen in the digester gas to ensure that there were no levels of oxygen that could affect the digestion process. The average O₂ composition measured was 1%, with a range of 0%-2% [Figs. 3.10(a and b)]. These quantities did not seem to affect the CH₄ composition in the biogas, or the other gases [Figs. 3.6(a and b)].

Fig. 3.6. (a) Effect of Fe₃O₄ addition on biogas composition; and (b) effect of FeCl₂ addition on biogas composition.
Fig. 3.7. (a) Effect of Fe$_3$O$_4$ addition on CH$_4$ fraction; (b) effect of FeCl$_2$ addition on CH$_4$ fraction; (c) EWMA model for CH$_4$; and (d) model residuals for CH$_4$.

Fig. 3.8. (a) Effect of Fe$_3$O$_4$ addition on CO$_2$ fraction; (b) effect of FeCl$_2$ addition on CO$_2$ fraction; (c) EWMA model for CO$_2$; and (d) model residuals for CO$_2$. 
Fig. 3.9. (a) Effect of Fe$_3$O$_4$ addition on N$_2$ fraction; (b) effect of FeCl$_2$ addition on N$_2$ fraction; (c) EWMA model for N$_2$; and (d) model residuals for N$_2$.

Fig. 3.10. O$_2$ in digester gas (a) when Fe$_3$O$_4$ was added to the reactor; and (b) when FeCl$_2$ was added to the reactor.
3.4 Conclusion

Facilities using BioMag® technology in their WWT processes and that continue to digest their sludge anaerobically can benefit from the presence of magnetite in the WAS. These facilities currently recover magnetite after the clarification process and before the WAS proceeds to the anaerobic digesters. This study investigated whether the magnetite used in this process could have some benefit in the AD process, in order to suggest recovery of the magnetite after AD to reap those benefits.

H₂S gas concentration decreased after adding magnetite to the anaerobic digester. The H₂S seemed to decrease with the increase in the dissolved magnetite iron, and vice versa. A 43% reduction in H₂S was achieved when the dissolved magnetite iron reached 1.38 mg/L. At this point, feeding of magnetite was discontinued and the H₂S decreased from 138 ppm to 79 ppm, which is below the 100-ppm level considered IDLH by OSHA. A further 6% reduction in H₂S gas occurred after magnetite feeding was stopped, which corresponded to a further increase in dissolved iron that could be explained by longer residence times of magnetite in the digester. The authors believe that higher levels of H₂S reduction could be achieved with continued operation of the digester with magnetite in the sludge, and depending on the quantities of magnetite added, and its residence time in the digester, because the solubility of magnetite also increased with the increase in contact time with water. This can be investigated further. The authors therefore suggest that instead of recovering magnetite after the sedimentation process, BioMag® facilities could consider magnetite recovery after AD. This would reduce the amount of sludge to be processed for magnetite recovery, and hence reduce recovery time and the load on recovery equipment, which could increase the service life and reduce the operation and
maintenance costs of the equipment. The addition of magnetite was stopped when
clogging problems arose; therefore, the authors also suggest designing a system that will
ensure adequate mixing of the digester contents, while accounting for magnetite addition.

No significant increase or decrease in the biogas volume or CH$_4$ composition in
the biogas was found with magnetite addition. On the other hand, after iron (II) chloride
was added to the digester, there was a slight increase in the gas volume with increase in
the dissolved iron concentration. This increase was due to higher CO$_2$ production, and a
reduction in CH$_4$ was seen during this period, which could be due to an inhibitory effect
of the elevated iron concentration on the methanogens. However, the H$_2$S gas was
removed completely from the digester within a short period after adding iron (II)
chloride, at which point the foul odor from the H$_2$S gas and the digestate had dissipated.
However, the dissolved iron concentration had reached 400 mg/L Fe which could be a
nuisance, because a reddish-brown precipitate quickly formed with the digestate after it
was exposed to air, and this could cause serious aesthetic and other problems, beyond the
AD process.

There also was an increase in the dissolved iron concentration due to magnetite
addition. The digester effluent reached a concentration of about 1.7 mg/L Fe after
magnetite addition had stopped. It is believed that this concentration could have increased
further with continued addition or operation of the digester with magnetite. The EPA
standard for iron in drinking water is 0.3 mg/L Fe, and levels above this have been said to
cause aesthetics problems due to precipitation of iron (III) and staining of plumbing,
laundry, utensils, and so forth, as well as plugging of irrigation equipment. There also
could be cost implications if the digester effluent is to be treated to reduce the iron levels before discharge, depending on the end use of the digester effluent.

The information in this study could help WWT facilities that have adopted BioMag® technology in their biological WWT processes and that continue to treat their WAS using AD, as well as other AD facilities that may be considering using magnetite to reduce H₂S in their biogas. The magnetite used in this study was that supplied for use in the BioMag® process, and therefore similar behavior is expected under similar reactor design and operation conditions to those in this study. The study is significant because H₂S gas can be highly toxic and can cause both acute and chronic illness in humans and can corrode metal and concrete equipment. Reduction of this gas implies reduced toxicity levels if inhaled, reduced cost of cleaning up the biogas before it can be used as a renewable source of energy, as well as reduced deterioration and cost of maintaining metal and concrete equipment if they corrode due to the presence of H₂S in the gas. This study could also inform WWT operators on what to expect if they choose to add magnetite to their AD processes and help them in decision-making processes pertaining to this.

Data Availability Statement

All the data, models, and code that support the findings of this study are available from the corresponding author upon reasonable request.

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CHAPTER 4
APPLICATION OF A THEORETICAL FRAMEWORK FOR UNDERSTANDING
SULFUR GRANULE FORMATION DURING THE ANAEROBIC DIGESTION
PROCESS³

Abstract

This research applies a previously validated bioenergetics model to determine whether the formation of elemental sulfur (S⁰) from hydrogen sulfide is thermodynamically possible during the anaerobic digestion (AD) process. The investigation was sparked by recent studies that reported that the presence of electronically conductive materials (e.g., magnetite) in the AD process could potentially facilitate elemental sulfur formation from hydrogen sulfide rather than the formation of ferrous sulfide (FeS), which is typically formed during the addition of iron salts (e.g., ferric chloride) into the AD environment for hydrogen sulfide control. The net Gibbs free energy change for the overall reaction resulting from the oxidation of hydrogen sulfide to elemental sulfur (S⁰) during the microbial conversion of organic matter to methane (CH₄) was estimated to be -9.90 kilojoules per mole of electrons transferred (kJ/mole e⁻). The exothermic characteristics of the overall bioenergetics reaction suggest that there may be a competitive growth advantage for anaerobic microorganisms that can establish themselves within the vicinity or region of electronically conductive materials. Based on the overall energy transfer estimated during S⁰ and CH₄ formation, a theoretical biomass yield (Y) of 0.097-grams of volatile suspended solids formed per gram of chemical oxygen demand removed (VSS/gram COD) was obtained. Given that the estimated theoretical Y is well within the range anticipated for facultative bacteria grown under
anaerobic conditions, the bioenergetics model appears to be well suited for predicting microbial reaction products from simple thermodynamic considerations. These present modeling results indicate that $S^0$ formation is theoretically possible during methane formation. However, reported experimental evidence suggests that the presence of an electron transfer shuttle is required to facilitate this reaction.

---

4.1 Introduction

Anaerobic digestion (AD) is a sludge stabilization process by which a consortium of facultative and obligate anaerobic bacteria transform complex organic compounds into methane (CH₄) and carbon dioxide (CO₂) gases, the primary components of biogas. In this stabilization process, the various microbial communities “communicate” with one another through facilitating various chemical changes in the aqueous environment. Microorganisms break down organic substrates in the absence of oxygen, producing biogas and more microbial cells. While biogas is composed of mainly methane (CH₄) and carbon dioxide (CO₂), other gases such as water vapor and hydrogen sulfide (H₂S) are present as well (USEPA 2021).

H₂S gas is produced when the anaerobic digester (ADR) influent contains sulfur compounds. While the presence of sulfates in the ADR, which are rapidly reduced to H₂S by sulfate reducing bacteria (SRB), is typically the primary source of H₂S found in biogas, other sulfur containing compounds (e.g., sulfites, thiols, etc.) can also serve as potential H₂S sources. When sulfate is the primary source of H₂S formation, organic substrates (e.g., acetate) or hydrogen (H₂) can be used as the electron donor (reducing agent) for SRB, with sulfate serving as the terminal electron acceptor (Metcalf and Eddy 2003; Ahmed and Rodriguez 2018).

Because methane is also formed through the processing of acetate and H₂ within the AD process, high sulfate concentrations in the AD influent can inhibit CH₄ formation due to substrate competition (Maillacheruvu et al. 1993; Metcalf and Eddy 2003; Madden et al. 2014). At concentrations greater or equal to 100 ppm, H₂S gas is considered immediately dangerous to life and health (IDLH) but could cause adverse health effects
at lower concentrations (OSHA 2005). H₂S can also attack ferrous and other metal surfaces as well as concrete (USEPA 1991).

H₂S gas can be removed from biogas using chemical scrubbers, iron sponges and other propriety methods (Saber and Takach 2009). Alternatively, H₂S gas production can be inhibited by the addition of iron salts to precipitate ferrous sulfide (FeS) (Ge et al. 2013; Park and Novak 2013; Lin et al. 2016; Zafar 2020; Ahn et al. 2021), and most recently, the use of electronically conductive materials like magnetite (Fe₃O₄) which have proven to reduce H₂S gas concentration in the biogas (Jung et al. 2020; Ayaa and McFarland 2021).

With Fe₃O₄ addition, it is reasonable to anticipate that sulfides could be precipitated as FeS. However, studies like Jin et al. (2019) and Jung et al. (2020) reported that they did not observe FeS formation when Fe₃O₄ was added to the digester. While Andriamanohiarisoamanana et al. (2018) suggested FeS precipitation as the mechanism of H₂S gas reduction when waste iron powder containing 85% Fe₃O₄ was added to the AD process, Jung et al. (2020) observed elemental sulfur (S⁰) formation as a possible mechanism for H₂S gas reduction. Jung et al. (2020) attributed the formation of elemental sulfur granules to direct interspecies electron transfer (DIET) between exoelectrogenic anaerobic sulfide oxidizing bacteria and electrotrophic methanogens, using Fe₃O₄ as an electron transfer conduit. Lupitskyy et al. (2018) who used zinc oxide nanowires instead of Fe₃O₄ also reported S⁰ formation in addition to the formation of zinc sulfide (ZnS). Zhou et al. (2016) suggested S⁰ as one of three potential pathways of H₂S removal when limonite was added to the anaerobic digester, the others being adsorption and FeS precipitation. From these studies therefore, it would seem that the presence of
electronically conductive materials such as magnetite, zinc oxide nanoparticles and limonite might facilitate the oxidation of sulfide to elemental sulfur during AD. The resulting oxidation of H₂S would generate reducing power that may contribute to other chemical transformations including the potential generation of methane formation.

While the addition of iron salts to the AD has been traditionally used to remove H₂S in biogas through FeS precipitation, the potential role of sulfur granule formation as a significant mechanism to remove H₂S from biogas through electronic transfer by conductive iron materials like Fe₃O₄, has barely been investigated. One of the first questions that must be answered regarding sulfur granule formation is whether such chemical species formation from H₂S is theoretically possible given the chemically reduced conditions characteristic of the AD environment. For redox reactions to result in specific end products whether catalyzed by chemicals and/or microorganisms, the overall reaction must be thermodynamically possible. In other words, the free energy change associated with the overall reaction(s) must be exothermic (a negative free energy change).

In this research, we evaluate the free energy changes associated with the formation of sulfur granules from H₂S and whether those reactions can yield sufficient energy to support growth of anaerobic microorganisms. The thermodynamic approach that we have selected is the bioenergetics model that has been developed and used in the wastewater industry to evaluate the biodegradation of recalcitrant organic compounds (McFarland and Sims 1991).
4.2 Methodology

4.2.1 Bioenergetics Model

The goal of this research was to use a simple bioenergetics model to determine if the reactions associated with the formation of sulfur granules under AD would theoretically support the growth of microorganisms.

Bioenergetics is a branch of biochemistry that investigates the flow of mass and energy through biological cells (IOMC 2021). Using bioenergetics, the Gibbs free energy change ($\Delta G^\circ$) of various half reactions is used to indicate whether energy is produced or consumed as reactants are converted to specific products. The superscript, $^\circ$, denotes that these values were calculated at standard conditions of temperature, 298 K, and pH = 7.0 (Metcalf and Eddy 2003). $\Delta G^\circ$ can be obtained from Eq. (4.1). The JANAF thermochemical tables (Stull and Prophet 1971) give values for the entropies and enthalpies of formation of various chemical constituents, and also provide information on how to use these data.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$  \hspace{1cm} (4.1)

Where:

$\Delta G^\circ$ = Gibbs free energy change of the reaction in kilojoules per mole of electrons

$\Delta H^\circ$ = enthalpy change of the reaction in kilojoules per mole of electrons

$\Delta S^\circ$ = entropy change in kilojoules per electron mole per Kelvin

$T$ = Temperature in Kelvin

A negative Gibbs free energy implies that energy is produced during this conversion and therefore, is theoretically beneficial to microbial growth. These types of reactions are termed exothermic, a term that reflects the fact that the reaction products are
at a lower energy level than reactants. A positive Gibbs free energy indicates that energy is not generated but, rather, is required as an input in order for the reaction to proceed (Metcalf and Eddy 2003; Doan et al. 2021). These reactions, termed endothermic, are characterized by reaction products that are at a higher energy level than reactants. The methodology for obtaining the Gibbs free energy change and calculating biomass yield was adopted from Metcalf and Eddy (2003) and is summarized in Fig. 4.1.

Other methods like Density Functional Theory (DFT) can also be used to calculate the entropies and enthalpies of formation of various chemical constituents (Benisek and Dachs 2018). The reference level used to calculate the enthalpy in the DFT approach, however, is 0 Kelvin (Benisek and Dachs 2018), while that in the JANAF thermochemical tables is 298 Kelvin (Stull and Prophet 1971; Metcalf and Eddy 2003). The enthalpies obtained from the DFT calculations therefore need to be transformed into standard enthalpies of formation at 298 Kelvin in order to make a direct comparison with the values in the JANAF thermochemical tables (Stull and Prophet 1971; Benisek and Dachs 2018). Also, the heat capacities used to calculate entropies in the DFT approach are at constant volume and need to be transformed to heat capacities at constant pressure to enable a direct comparison of the entropies obtained from DFT calculations to those in the JANAF thermochemical tables (Benisek and Dachs 2018).
4.2.2 Identifying the Reacting Species and Calculating the Net Gibbs Free Energy

The first step in evaluating sulfur granule formation during the AD process was to identify the list of chemical half reactions that would contribute to the formation of the reaction products (i.e., CH$_4$, CO$_2$ and S$^0$) from the reactants (organic matter and various sulfur-based compounds). These half reactions are then used to build an overall reaction from which the net Gibbs free energy change can be computed. The half reactions chosen
in this study represent the AD of whey (i.e., milk protein), which is comprised of a number of sulfur-based amino acids. Whey was chosen to simulate the study by Jung et al. (2020) who observed S\(^0\) formation when whey protein was used as the organic substrate.

There are four important half reactions to consider in this process which include the mineralization of whey protein, Eq. (4.2). The next half reaction of importance is the formation of methane, which is represented by Eq. (4.3). The final two half reactions that comprise the overall reaction include the mineralization of H\(_2\)S and the reduction of sulfate to elemental sulfur represented by Eqs. (4.4) and (4.5), respectively. The free energy changes, i.e., \(\Delta G^0\) for all half reactions were collected from standard thermodynamic tables (McCarty 1975; Metcalf and Eddy 2003). The net Gibbs free energy change associated with the overall chemical reaction (\(\Delta G_R\)) can be obtained by positioning the half reactions so that all of the anticipated reactants are placed on the left hand-side and all of the anticipated products are placed on the right hand side. The equations can then be added to ensure elimination of any free electrons.

\[
\frac{1}{66}C_{16}H_{24}O_5N_4 + \frac{27}{66}H_2O \rightarrow \frac{8}{33}CO_2 + \frac{2}{33}NH_4^+ + \frac{31}{33}H^+ + e^-; \quad \Delta G^0 = -32.22 \text{ kJ/mole } e^- \quad (4.2)
\]

\[
\frac{1}{8}CO_2 + H^+ + e^- \rightarrow \frac{1}{8}CH_4 + \frac{1}{4}H_2O ; \quad \Delta G^0 = 24.11 \text{ kJ/mole } e^- \quad (4.3)
\]

\[
\frac{1}{16}H_2S + \frac{1}{16}HS^- + \frac{1}{2}H_2O \rightarrow \frac{1}{8}SO_4^{2-} + \frac{19}{16}H^+ + e^- ; \quad \Delta G^0 = -21.27 \text{ kJ/mole } e^- \quad (4.4)
\]

\[
\frac{1}{6}SO_4^{2-} + \frac{4}{3}H^+ + e^- \rightarrow \frac{1}{6}S + \frac{2}{3}H_2O ; \quad \Delta G^0 = 19.48 \text{ kJ/mole } e^- \quad (4.5)
\]

Where:

kJ = kilojoules

mole e\(^-\) = mole of electrons
4.2.3 Fraction of Substrate Converted to Cell Tissue and Fraction Converted to Energy

Approximately, 40% to 80% of the energy generated from the microbial oxidation of an organic substrate is captured by the cell to support its growth and maintenance needs (McCarty 1971; McFarland and Sims 1991; Metcalf and Eddy 2003). The remainder of the energy generated is lost as heat that is discharged into the environment. To account for this systemic loss of chemical energy by the microbial cell, the efficiency of biological energy capture \((K)\) is assumed to be 60% or 0.60 within the bioenergetics model (McCarty 1971; McFarland and Sims 1991).

The intrinsic value of the bioenergetics model is that it not only determines if a potential set of reactions are thermodynamically favorable, but it can also be employed to estimate the theoretical cell growth or yield \((Y)\). If cell tissue were measured as volatile suspended solids (VSS) and the organic substrate concentration were measured as chemical oxygen demand (COD), \(Y\), can be reported in units of grams VSS per gram COD.

In the bioenergetics model, it is assumed that a fraction of the organic substrate removed by the microbial cell is synthesized into cell tissue (represented as an increase in volatile suspended solids or VSS) while the remaining fraction of substrate is oxidized to produce required maintenance energy. These two parameters, which are designated as \(f_s\) (synthesis) and \(f_e\) (energy) within the model, have the units of grams COD converted to cell tissue per gram of COD removed (i.e., grams COD_{cells}/gram COD removed) and grams COD converted to energy per gram of COD removed (i.e., gram COD_{energy}/gram COD removed), respectively.
For the fraction of organic substrate used to synthesize cell mass (i.e., $f_s$), it is assumed that the organic substrate must first be converted to a three (3) carbon compound, i.e., pyruvic acid (or pyruvate), which is an important chemical intermediate associated with multiple biological reactions (McCarty 1971). The Gibbs free energy change associated with converting the organic substrate to pyruvate ($\Delta G_P$) can be positive or negative depending on the organic substrate chemical complexity and energy state. For example, conversion of glucose (a six-carbon substrate) to pyruvate will yield a negative ($\Delta G_P$), meaning that energy is generated during this reaction while conversion of methane (a one carbon organic substrate) to pyruvate will yield a positive ($\Delta G_P$) which suggests that an energy input is required to facilitate this reaction. The pyruvate mineralization half reaction that is utilized to convert any organic substrate to pyruvric acid is given by Eq. (4.6).

$$\frac{1}{5}CO_2 + \frac{1}{10}HCO_3^- + H^+ + e^- \rightarrow \frac{1}{10}CH_3COCOO^- + \frac{2}{5}H_2O ; \ \Delta G^o = 35.78 \ kJ/mole \ e^-$$ (4.6)

The bioenergetics model assumes that the Gibbs free energy change associated with the conversion of one electron equivalent of pyruvate to cell mass ($\Delta G_C$) is constant and is equal to +31.41 kJ per mole of electrons transferred (McCarty 1971). The final chemical consideration in the bioenergetics model is oxidation state of the nitrogen source utilized in cell synthesis ($f_s$). Nitrogen may be available as nitrate, nitrite, elemental nitrogen, or ammonia. The bioenergetics model assumes that the oxidation state of nitrogen required for cell synthesis is that of ammonia. In other words, if a nitrogen source other than ammonia were being utilized for cell synthesis, it first must be reduced to ammonia through chemical reduction, a process that results in a positive Gibbs
free energy change ($\Delta G_N$). In other words, energy is consumed to reduce oxidized forms of nitrogen to ammonia. For example, if nitrate (NO$_3$) were the only nitrogen source available, the Gibbs free energy change for converting one electron equivalent of NO$_3$ to ammonia is estimated to be $+17.46$ kJ per mole of electrons (McCarty 1971). Similarly, the Gibbs free energy change to reduce one electron equivalent of nitrite (NO$_2$) or elemental nitrogen (N$_2$) to ammonia is $+13.61$ kJ and $15.85$ kJ per mole of electrons, respectively (McFarland and Sims 1991).

Within the strongly reduced chemical environment associated with AD, it is assumed that the available nitrogen for cell synthesis is already at the oxidation state of ammonia and therefore the free energy change required for nitrogen reduction ($\Delta G_N$) equals zero (0). Given these assumptions, the Gibbs free energy change associated with production of one electron equivalent of cells ($\Delta G_S$) may be represented by Eq. (4.7).

$$\Delta G_S = \frac{\Delta G_P}{Km} + \Delta G_c + \frac{\Delta G_N}{K}$$

(4.7)

Where:

- $\Delta G_S$ = Gibbs free energy change associated with production of one electron equivalent of cells
- $K$ = fraction of energy captured by the cell (0.6)
- $\Delta G_P$ = Gibbs free energy associated with converting one electron equivalent of the organic substrate to pyruvate
- $m = -1$ if $\Delta G_P$ is negative and $+1$ if $\Delta G_P$ is positive
- $\Delta G_c = +31.41$ kJ per electron equivalent of cells
- $\Delta G_N = 0$

### 4.2.4 Calculating Cell Yield

For a microbial process to be sustainable, a sufficient amount of energy must be generated during the overall oxidation of the organic substrate ($\Delta G_R$) to support both cell synthesis ($f_i$) as well as the cells maintenance energy needs ($f_e$). In the AD process, the overall oxidation of the organic substrate generates CO$_2$, H$_2$O and CH$_4$. However, in the
current application of the bioenergetics model, the oxidation of H\textsubscript{2}S and simultaneous reduction of sulfate are superimposed on this basic microbial process.

Based on the bioenergetics model definitions, an independent mass and energy relationship can be developed to estimate cell yield (Eqs. (4.8) and (4.9)). The first relationship, Eq. (4.8), is a simple energy balance that states that the ratio of energy required for cell synthesis (\(\Delta G_s\)) to energy captured by the cell (\(K \Delta G_R\)) is equal to the ratio of the fraction of substrate that goes to energy over the fraction of substrate that goes to cell synthesis (\(f_e/f_s\)). The second relationship, Eq. (4.9), is a simple mass balance that states that the fraction of substrate that goes to energy production (\(f_e\)) plus the fraction of substrate that goes to cell synthesis (\(f_s\)) is equal to one (Metcalf and Eddy 2003).

\[
\frac{f_e}{f_s} = \frac{-\Delta G_s}{K \Delta G_R} \tag{4.8}
\]

\[
f_e + f_s = 1.0 \tag{4.9}
\]

Given these two independent equations, it is possible to solve for the two unknowns (i.e., \(f_e\) and \(f_s\)) using the information from the chemical half reactions and employing the bioenergetics model assumptions. Determination of the fraction of organic substrate that results in cell synthesis (\(f_s\)) allows the estimation of the microbial cell yield (\(Y\)). To accomplish this step, an assumption must be made of the chemical formula of microbial cell tissue. If it were assumed that microbial cell tissue had the chemical formula of C\textsubscript{5}H\textsubscript{7}O\textsubscript{2}N, the chemical oxidation demand (COD) of cell tissue may be estimated using Eq. (4.10).

\[
\begin{align*}
\text{C}_{5}\text{H}_{7}\text{O}_{2}\text{N} + 5\text{O}_2 & \rightarrow 5\text{CO}_2 + \text{NH}_3 + 2\text{H}_2\text{O} \\
\end{align*} \tag{4.10}
\]
Given a molecular weight of cell tissue of 113 grams per gram-mole and an oxygen demand of 160 grams of molecular oxygen \((5 \times 32)\) per gram-mole of cell tissue, the COD equivalent of cell tissue is 1.42-grams COD\(_{\text{cells}}\) per gram VSS (i.e., 160 grams of Oxygen/113 grams of VSS). Using this COD equivalent of cell tissue and the definition of \(f_s\), microbial yield \((Y)\) can be estimated using Eq. (4.11).

\[
Y = \frac{f_s}{1.42 \frac{\text{gram COD}_{\text{cells}}}{\text{gram VSS}}} = \frac{\frac{\text{gram COD}_{\text{cells}}}{\text{gram VSS}}}{1.42 \frac{\text{gram COD removed}}{\text{gram VSS}}} = \frac{\text{gram VSS}}{\text{gram COD removed}}
\]

(4.11)

4.3 Results and Discussion

4.3.1 Sulfur Formation

The overall reaction for the oxidation of sulfide to \(S^0\) is given in Eq. (4.12), which was derived by combining Eqs. (4.4) and (4.5). This reaction has a negative Gibbs free energy, \(\Delta G^0_{\text{Sulfur}} = -1.79 \text{ kJ/mol e}^-\), which implies that the reaction generates energy (exothermic) that may be utilized by microbes for cell tissue growth and/or maintenance needs. This theoretical result supports the laboratory results reported by Jung et al. (2020), Lupitskyy et al. (2018), and Zhou et al. (2016) who observed reduction in \(H_2S\) in the digester biogas along with sulfur granule formation in the presence of \(Fe_3O_4\), zinc oxide nanoparticles, and limonite, respectively.

\[
\frac{1}{16} H_2S + \frac{1}{16} HS^- + \frac{1}{24} SO_4^{2-} + \frac{7}{48} H^+ \rightarrow \frac{1}{6} S + \frac{1}{6} H_2O ; \Delta G^0_{\text{Sulfur}} = -1.79 \text{ kJ/mol e}^- \tag{4.12}
\]

A possible explanation for the formation of \(S^0\) instead of FeS precipitation could be the low aqueous solubility of \(Fe_3O_4\) which would imply less bioavailability. Jung et al. (2020) suggested DIET between the exoelectrogenic sulfide oxidizing bacteria and electrotrophic methanogens. DIET is a recent discovery in which syntrophic microbial
species in anaerobic environments, for example, are believed to exchange electrons
directly without the help of electron shuttles like hydrogen through interspecies hydrogen
transfer (IHT), which is believed to be a very slow process (Viggi et al. 2014; Dube and
Guiot 2015; Liu et al., 2019). Some recent studies therefore added conductive materials
like Fe$_3$O$_4$ to the AD process to enhance this phenomenon to improve methanogenesis.
As a result, some of these studies reported an increase in the methane production rate,
and/or methane yield, and suggested that this was due to DIET between the
exolelectrogenic microbes and methane formers (Viggi et al. 2014; Jin et al. 2019; Liu et
al., 2019). This energy transfer, which is believed to be facilitated by the electronically
conductive Fe$_3$O$_4$, could also easily explain S$^0$ formation. Lupitskyy et al. (2018) who
added zinc oxide nanowires as an electronically conductive material in the AD
environment suggested S$^0$ formation and sulfide (ZnS) precipitation as the primary
mechanisms for H$_2$S removal from biogas. Alternatively, Zhou et al. (2016) added
limonite (i.e., hydrated ferric oxide) to their digesters. Their results suggested that S$^0$
granule formation, ferric sulfide (FeS) precipitation and H$_2$S adsorption were the primary
mechanism(s) of H$_2$S removal from biogas.

4.3.2 Overall Energy Production

The overall microbial oxidation of whey protein (C$_{16}$H$_{24}$O$_5$N$_4$) to produce CH$_4$,
CO$_2$ and S$^0$ within the AD environment was derived by adding Eqs. (4.2), (4.3), (4.4) and
(4.5) with the resulting reaction summarized in Eq. (4.13). The net Gibbs free energy
associated with this overall reaction ($\Delta G_R$) is -9.90 kJ per mole of electrons transferred.
This result implies that the microbial cell can generate useful energy required for growth
and/or maintenance by facilitating this chemical reaction.
The reaction of whey protein to generate pyruvate was obtained by adding Eqs. (4.2) and (4.6) with the result summarized in Eq. (4.14). The free energy change $\Delta G_P$ associated with this reaction is $+3.56$ kJ per mole of electrons transferred ($m = +1$). This result indicates that pyruvate formation from whey protein is endothermic and requires a net input of energy to proceed.

$$\frac{1}{66}C_{16}H_{24}O_5N_4 + \frac{1}{16}H_2S + \frac{1}{16}HS^- + \frac{1}{24}SO_2^{2-} + \frac{109}{528}H^+ \rightarrow \frac{1}{8}CH_4 + \frac{1}{6}S + \frac{31}{264}CO_2 + \frac{76}{10000}H_2O + \frac{2}{33}NH_3^+; \Delta G_R = -9.90 \text{ kJ/mole e}^- \quad (4.13)$$

### 4.3.3 Cell Yield

The reaction of whey protein to generate pyruvate was obtained by adding Eqs. (4.2) and (4.6) with the result summarized in Eq. (4.14). The free energy change $\Delta G_P$ associated with this reaction is $+3.56$ kJ per mole of electrons transferred ($m = +1$). This result indicates that pyruvate formation from whey protein is endothermic and requires a net input of energy to proceed.

$$\frac{1}{66}C_{16}H_{24}O_5N_4 + \frac{1}{10}HCO_3^- + \frac{2}{33}H^+ + \frac{1}{110}H_2O \rightarrow \frac{7}{165}CO_2 + \frac{2}{33}NH_3^+ + \frac{1}{10}CH_3COCOO^-; \Delta G_P = 3.56 \text{ kJ/mole e}^- \quad (4.14)$$

Substituting the known and estimated values for $\Delta G_P$, $\Delta G_C$, $\Delta G_N$, $K$ and $m$, $\Delta G_S$ was calculated as $37.34$ kJ per mole of electrons transferred (Eq. (4.7)). Similarly, substituting these values into Eqs. (4.8) and (4.9) resulted in estimates of the fraction of substrate converted to cell tissue and fraction of substrate converted to energy as $f_s = 0.137$ and $f_e = 0.863$, respectively. Finally, substituting the value of $f_s$ into Eq. (4.11) resulted in an estimated cell yield ($Y$) of approximately 0.097-gram VSS produced as cell tissue per gram of COD removed.

The cell yield of 0.097-gram VSS per gram COD removed is a reasonable estimate of the type of yield expected within a facultative/anaerobic environment (McCarty 1971). Metcalf and Eddy (2003) also suggest that the range for the overall combined cell yield for fermentation and methanogenesis should be 0.05-0.10-gram VSS/gram COD. Therefore, based on the results of the bioenergetics model summarized
in Table 4.1, simultaneous sulfate reduction and H$_2$S oxidation to elemental sulfur is thermodynamically possible within the AD environment. From reported laboratory results, it appears that the formation of sulfur granules can only occur if there exist electronically conductive materials within the AD environment that facilitate electron transfer between various microbial species.

Table 4.1. Summary of results from the bioenergetics model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta G^\circ_{Sulfur}$</td>
<td>kJ/mole of electrons</td>
<td>-1.79</td>
</tr>
<tr>
<td>$\Delta G_R$</td>
<td>kJ/mole of electrons</td>
<td>-9.90</td>
</tr>
<tr>
<td>$K\Delta G_R$</td>
<td>kJ/mole of electrons</td>
<td>-5.94</td>
</tr>
<tr>
<td>$\Delta G_P$</td>
<td>kJ/mole of electrons</td>
<td>3.56</td>
</tr>
<tr>
<td>$\Delta G_S$</td>
<td>kJ/mole of electrons</td>
<td>37.34</td>
</tr>
<tr>
<td>$f_e$</td>
<td>gram COD$_{energy}$/ gram COD removed</td>
<td>0.863</td>
</tr>
<tr>
<td>$f_s$</td>
<td>gram COD$_{cells}$/ gram COD removed</td>
<td>0.137</td>
</tr>
<tr>
<td>$Y$</td>
<td>gram VSS/gram COD removed</td>
<td>0.097</td>
</tr>
</tbody>
</table>

4.4 Conclusion and Significance

Using a peer-reviewed bioenergetics model, it was demonstrated that it is thermodynamically possible for sulfate reduction and H$_2$S oxidation to result in the formation of sulfur granules during the AD process. The overall reaction resulting in sulfur formation had a negative Gibbs free energy, indicating that a microbial cell associated with these transformations could generate useful energy for growth and/or maintenance.

While the bioenergetics model demonstrated that sulfur granule formation was thermodynamically possible, the model does not take into account the level of activation
energy needed to bring the reactants (organic substrate, sulfate, H$_2$S) to a sufficient energy state to initiate the overall reaction. Laboratory studies suggest that sulfur granule formation was only detected when Fe$_3$O$_4$, zinc oxide nanoparticles or other electronically conductive material was present. These few studies suggest that these and perhaps other conductive materials may act as catalyst in sulfur granule formation by facilitating electron transfer between various microbial species.

Because the formation of sulfur granules under AD conditions was found to be an exothermic reaction, energy is released that could potentially support microbial growth. In other words, the fact that energy is generated during the sulfur granule formation process suggests that some of that energy may be utilized in the polymerization of whey protein into microbial cell tissue. Assuming a chemical formula for the organic fraction of cell tissue as C$_5$H$_7$O$_2$N, a cell yield of 0.097 grams VSS per gram COD removed was estimated using the bioenergetics model. The fact that the cell yield is within the reasonable range of what would be expected for a facultative/anaerobic microbial community lends greater support that sulfur granule formation under AD conditions is feasible.

This is the first study, to the best of our knowledge, to conclusively demonstrate that the formation of sulfur granules from the simultaneous reduction of sulfate and oxidation of H$_2$S under AD conditions is thermodynamically feasible. While most studies have focused on the formation of FeS for removal of H$_2$S from biogas, this study suggests that commingling of electronically conductive materials such as Fe$_3$O$_4$, zinc oxide nanoparticles or other materials (e.g., carbon nanoparticles) within the AD influent could remove H$_2$S without the formation of FeS.
Formation of elemental sulfur would imply a reduction in the hydrogen sulfide in the biogas produced. This would reduce the corrosivity of the gas to concrete and metal components within the gas distribution system, reducing operation, maintenance, and/or replacement costs of these components. It would also reduce costs of gas clean up before the biogas can be used as a renewable energy source, as well as reduce its toxicity to operators at these facilities when they are exposed to the gas.

From a sludge quality and beneficial use standpoint, FeS in the AD restricts the availability of sulfur to crops if the final sludge product is recycled on agricultural or forest land. In other words, the solubility product ($K_{sp}$) of ferrous sulfide is low ($4 \times 10^{-19}$), which means little sulfur is available for plant uptake if the sludge is used as a slow-release crop fertilizer. On the other hand, if sulfur granules are available within the recycled sludge, they will readily solubilize in the soil water matrix and become available for crop uptake and growth (McFarland 2001).

Although a limited number of research studies have reported sulfur granule formation with the use of electronically conductive materials in laboratory experiments, further research should be conducted to confirm the role of electron transfer catalysis on elemental sulfur formation under anaerobic conditions. Moreover, it is vital to investigate the scalability of the bench-scale observations to full-scale anaerobic digester operations. Of particular importance is the verification that the presence of electronically conductive materials does not impede or otherwise reduce methane gas production yields during sludge treatment operations.
The potential for use of anaerobic sludge as a potential sulfur source would be attractive to farmers, ranchers, landscapers and other agricultural producers. Sulfur is a critical nutrient required for crop growth and its availability in soil is of paramount importance to sustaining crop yields and quality (TSI 2022). Particulate or granular sulfur in land applied sludge could easily be converted to sulfate-sulfur by microorganisms in the soil, making it available for plant uptake (Mosaic 2022). This would reduce the financial cost of sulfur-based fertilizers while maintaining high crop yields.

Data Availability Statement

No data, models, or code were generated or used during this study.

Acknowledgments

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References


CHAPTER 5
SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

The use of magnetite, an iron oxide mineral, in MWWT has piqued the interest of some WWT operators around the country as they seek to address the challenge of high nitrogen and phosphorus in the effluent discharge from their facilities, in order to meet tighter nutrient effluent limits imposed by regulatory authorities, and to protect the environment. A technology called BioMag® which adds magnetite to the secondary WWT process at biological WWT facilities is being adopted by some facilities to address this challenge. However, there are facilities that have been hesitant to adopt this technology because it is still relatively new, and they do not fully understand the nutrient removal mechanisms of this technology, due to limited literature resources and a limited track record on magnetite use in MWWT. This dissertation, therefore, sought to assess the effectiveness of magnetite in MWWT and on the downstream anaerobic digestion process in order to furnish WWT operators with a more complete information source that can help them make more informed decisions pertaining to the use of the magnetite technology. The motivation for this research stemmed from the decision by the City of Logan, UT, to adopt the BioMag® technology to enable them to meet more stringent effluent total phosphorus and ammonia requirements imposed by the Utah Division of Water Quality.

In Chapter 2, the effect of the magnetite technology upgrade on N and P removal at the Marlay-Taylor WRF in Maryland was estimated using intervention analysis. Results revealed that the effluent TN and TP reduced by 98% and 77%, respectively, since the technology upgrade and that the facility is meeting its WLA requirements for these pollutants. The SVI and MLSS which are important operating parameters improved
and were within acceptable limits. The facility is also currently able to treat wet weather flows higher than its design capacity while still meeting discharge effluent requirements, which indicates capacity expansion. The potential mechanisms of N and P removal were also explained in this chapter. While the reduction in TN could be attributed entirely to the magnetite technology, the reduction in TP could not. This is because the facility is also adding ferric salts to the process to improve phosphorus removal. Therefore, it seems that the magnetite technology is very effective in N removal but its effectiveness in P removal while acting independently without the assistance of other P removal methods is unclear. Chemical addition is necessary at the Marlay-Taylor WRF to enhance P removal, most likely because the four-stage Bardenpho activated sludge system, which is the configuration of the bioreactors at the Marlay-Taylor WRF is designed for N removal.

In comparison, the City of Logan, UT, will be using the three-stage Bardenpho activated sludge system, which is designed for P as well as N removal. This configuration has an anaerobic zone at the beginning of the reactor system, which is essential for a biological P removal process. It is therefore expected that the new Logan City wastewater treatment facility should be able to effectively remove P without additional chemicals. This is because the mechanisms of nutrient removal by the magnetite are attributed to an increase in the active biomass in the system, which are the microbes that do the work of treating the wastewater, as well as enhanced clarification which will reduce the P tied to the suspended solids in the effluent. Care should be taken, however, to ensure that there is enough food for the microbes in the system. Higher biomass populations will require higher amounts of substrate in the form of readily biodegradable organic matter, which they can use for growth and/or cell maintenance. Hence, an adequate food to
microorganism ratio will need to be maintained. It will therefore be interesting to compare the data from Logan City with that from Marlay-Taylor, once it is available.

The information presented in this section could help wastewater treatment operators make more informed decisions pertaining to the adoption or use of the magnetite technology at their facilities. Additional research on the BioMag® magnetite’s effectiveness on P removal alone could be conducted. This information could help facilities struggling with mainly P removal to make more informed decisions as they contemplate on whether to adopt the technology. Overall, the information presented shows that the magnetite technology upgrade has helped the Marlay-Taylor WRF to meet their nutrient removal goals and comply with regulatory requirements, and to also avoid penalties for non-compliance with their waste load allocation (WLA) requirements, which they paid before the upgrade.

A novel approach to the forecasting methodology in the intervention analysis model that was originally developed by Box and Tiao (1965, 1975) was also proposed in Chapter 2, where both the time series before and after the intervention (the magnetite technology upgrade) were forecast forward, as opposed to the original intervention analysis model which proposes a backward forecast of the time series after the intervention. The proposed forward forecast should give better predictions when the data series before the intervention has minimal drift and the data series after the intervention has a larger drift followed by a gradual move to stability, as described in the chapter. This would give the data further away from the intervention, in the post-upgrade time series, higher weights and would account for a fuller effect of the intervention. It is therefore recommended that a proper assessment of the time series is made before applying the intervention analysis model, in order to determine whether to predict the data series
forward or backward. This would enable more realistic estimates and ultimately better decisions to be made, as small changes in predictions could result in significantly higher implementation costs on certain projects.

In Chapter 3, the effect of magnetite on the anaerobic digestion process was evaluated. The same magnetite in the same proportions proposed for the BioMag® process was added to the digesters. Results showed that there was no significant difference in methane production and in the gas volume, but a significant decrease in the concentration of the hydrogen sulfide gas was obtained. The hydrogen sulfide gas concentration decreased by 49% (from 138 ppm to 70 ppm). A concentration of 70 ppm is below the level stipulated to be immediately dangerous to life and health (IDLH) by the Occupational Health and Safety Administration (OSHA) which implies decreased toxicity to humans. The hydrogen sulfide gas concentration was, however, expected to decrease further with continued magnetite addition to the digester. Reduced levels of hydrogen sulfide in the biogas could also reduce its corrosivity to metal and concrete components within the gas distribution system, thereby increasing their lifespan and reducing maintenance and replacement costs of the equipment.

The addition of magnetite during these experiments was stopped when clogging problems arose in the tubes circulating the digester contents. This could be attributed to the accumulation of magnetite in the digester and thickening of the sludge, which could affect the mixing of the digester contents, yet adequate mixing is important to achieve optimum performance of the digesters (Metcalf and Eddy 2003; Riffat 2013). It is therefore recommended that anaerobic digesters intending to operate with magnetite have an adequate design that accounts for the inclusion of magnetite, especially with the
pumping and circulation system, in order for the system to operate efficiently, and without interruptions.

The dissolved iron in the digester was measured and it reached 1.7 mg/L after magnetite addition to the digester had stopped. At this level, the iron can precipitate and cause aesthetic problems, staining of plumbing, as well as plugging of micro-irrigation equipment. It is expected that the dissolved iron concentration would increase with the continued addition of magnetite. These levels of iron in the digester could pose a problem, as the effluent might need to be treated to remove the iron depending on its intended use, which would come at a cost.

Due to the benefit of the magnetite in the reduction of the toxic H₂S gas which can be corrosive to equipment and toxic to humans, it is recommended that wastewater treatment facilities using BioMag® and anaerobic digestion for sludge stabilization, recover the magnetite from the process after anaerobic digestion instead of after the sedimentation process in the final clarifiers. This will reduce the loading on the magnetite recovery equipment and increase its lifespan, or even reduce the cost of procuring this equipment as they may require fewer or smaller-sized equipment. Further research could however be done to assess the effect of much lower proportions of the magnetite in the anaerobic digester since facilities are currently recovering about 95% of the magnetite. This implies that only about 5% would remain in the waste sludge and proceed to the digesters. This alternative and its implications could also be evaluated, and the opportunity cost determined to help facilities make better decisions. The effect and implications (cost and otherwise) of the dissolved iron in the effluent from the anaerobic digesters should also be included in these evaluations.
Chapter 4 aimed at investigating the possibility of elemental sulfur formation during the anaerobic digestion process. Many studies that have added iron compounds to the AD process to reduce hydrogen sulfide in the anaerobic digester have reported precipitation of iron sulfide (FeS) as the removal mechanism. Recent studies, however, that added conductive materials to the digester reported elemental sulfur formation as the removal mechanism of the hydrogen sulfide. This study, therefore, sought to determine if it is theoretically possible for hydrogen sulfide to be oxidized to elemental sulfur under anaerobic conditions. A bioenergetics model was used to determine if the overall reaction leading to sulfur formation was thermodynamically possible. Results indicated that this reaction was exothermic, with a Gibbs free energy change of -9.90 kJ/mole e\textsuperscript{-} and a biomass yield of 0.097-gram VSS/gram COD, implying that energy was produced, which could support the growth of microorganisms. Microorganisms are important in any biological process as they drive the reactions. The cell yield obtained is within the reasonable range expected for a facultative/anaerobic microbial community (McCarty 1971), which provides support to the feasibility of sulfur granule formation under AD conditions.

Although the bioenergetics model revealed that sulfur granule formation was thermodynamically possible under AD conditions, it does not account for the level of activation energy needed to bring the reactants (organic substrate, sulfate, H\textsubscript{2}S) to a sufficient energy state to initiate the overall reaction. From laboratory studies that observed sulfur granule formation during AD experiments, it appears that this was only possible when conductive materials like magnetite, limonite, and zinc oxide nanoparticles were added to the digesters. Therefore, it seems like conductive materials may be a necessary catalyst in the formation of sulfur granules by facilitating electron transfer.
between various microbial species (Yang et al. 2018; Jung et al. 2020; Ayaa and McFarland 2021).

This is the first study, to the best of our knowledge, to conclusively demonstrate that it is thermodynamically feasible to form sulfur granules from the simultaneous reduction of sulfate and oxidation of H\(_2\)S under AD conditions. The study suggests that commingling of electronically conductive materials within the AD influent could remove H\(_2\)S without the formation of FeS.

This finding is important because the use of magnetite and other conductive materials for H\(_2\)S control in anaerobic digesters may be a safer option than methods such as air or oxygen addition to the digesters. Oxygen could hinder the activity of some obligate anaerobes in anaerobic digesters. Also, this could be an important source of sulfur as a fertilizer in the biosolids from the digester when land applied to agricultural fields. Sulfur is more soluble than sulfide (FeS) in water and therefore would be taken up more easily by plants for growth.

In conclusion, the use of magnetite in municipal wastewater treatment for biological nutrient removal of nitrogen and phosphorus is still a relatively new technology. The information presented in this dissertation could help municipal wastewater treatment operators considering using magnetite, as well as those that have newly adopted the technology, like the City of Logan, UT, to have a better understanding of the BioMag® magnetite technology, manage expectations, and make more informed decisions pertaining to the inclusion of magnetite in their treatment processes.
References


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EDUCATION

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Civil Engineering Jan 2009
Senior Year Project: Analysis of Pavement Response Due to Traffic Loading along Mary Stuart Road
Advisor: Dr. Umaru Bagampadde

CERTIFICATIONS

OSHA 40-Hour HAZWOPER Certification – USU, Logan, UT Apr 2017
Engineer in Training (E.I.T.) – Utah Apr 2012

COMPUTER SKILLS

Microsoft Office, AutoCAD, ArcGIS, R, HEC-RAS, HEC-HMS

LEADERSHIP

President May 2011 - May 2012
National Society of Black Engineers (NSBE), USU Chapter, Logan, UT
➢ Increased society membership and participation in activities and competitions at the chapter, regional and national levels
➢ Fundraised to ensure that all members attended both the regional and national conferences
➢ Led a group of students to USU’s first NSBE Consulting Design Olympiad (CDO) competition and took first place
➢ Encouraged students to participate in other NSBE competitions such as the Technical Research Exhibition (TRE), where they presented their academic research, and also organized students to support the participants
➢ Organized students to participate in events around campus, such as Engineering Week, community outreach mentorship programs, and the homecoming street painting competition at USU
➢ Had the first USU representative voted to serve on the NSBE Region 6 Regional Executive Board (REB), as the Mountain Zone chairperson for the next academic year

Student Class Representative 2005 - 2008
Makerere Engineering Society (MES), Makerere University, Kampala

➢ Acted as a liaison between the MES executive board and the civil engineering class
➢ Encouraged students to register and become paid members of the society
➢ Informed the class of meetings and activities/events organized by the student board and encouraged them to participate

RESEARCH EXPERIENCE

Graduate Research Assistant Jan 2017 - Dec 2021
UWRL, USU, Logan, UT
➢ Investigated and proved, using a bioenergetics model, that it was theoretically possible to form elemental sulfur under anaerobic digestion conditions
➢ Conducted anaerobic digestion laboratory experiments to determine the effect of magnetite on hydrogen sulfide gas production which can be toxic to humans, as well as its effect on biogas production, on the digester effluent, and on digester operation
➢ Evaluated the effectiveness of magnetite in wastewater treatment, which was seen to improve effluent water quality and the operating parameters at a facility, and in the process, devised a modified approach to the data analysis procedure to improve data forecasting

Research Associate Apr 2012 - Nov 2014
BioInnovations Center, Biological Engineering Department, USU, Logan, UT
➢ Assisted in managing the laboratory, including, ensuring that health and safety procedures were followed, and making timely purchases for materials and equipment needed to ensure that all students’/employees’ research proceeded smoothly
➢ Investigated a methodology to separate lignin from black liquor
➢ Developed a technology to produce high surface area activated carbon from lignin and coconut shells, with good adsorption properties, making it attractive for use as an adsorbent in the water/wastewater treatment industry
➢ Trained and operated on pyrolysis equipment to produce bio-oil from different types of wood biomass
Graduate Research Assistant Jan 2010 - Dec 2011
UWRL, USU, Logan, UT
➢ Tested the algorithm of a model that is currently being used by the Institutional Framework managing the Senegal River (the OMVS) to allocate costs and benefits from the use of the river equally and equitably among the basin countries (Senegal, Mali, Mauritania and Guinea), in sectors such as agriculture, hydropower production, mining, navigation, and municipal and industrial uses
➢ Reviewed and compared various Institutional Frameworks managing International Rivers in Africa and Asia and the methods of conflict resolution employed in sharing the water resource

Research Assistant 2007 - 2008
Supervisor: Dr. Gaddi-Ngirane Katashaya, Deputy Dean, Office of Research and Higher Degrees, Faculty of Technology, Makerere University
➢ Conducted research to evaluate the course content in the civil engineering curriculum by administering questionnaires to past graduates

TEACHING AND MENTORSHIP EXPERIENCE

Teaching Assistant Spring 2019¹ and 2020²
USU, Logan, UT
➢ Assisted in teaching a class in biological processes in wastewater treatment to graduate students, including preparing and grading assignments¹ &²
➢ Assisted in teaching a class in physical and chemical processes in water treatment to graduate students, including preparing and grading assignments²

Assistant Lecturer Aug - Dec 2015
Ndejje University, Kampala, Uganda
➢ Taught 3rd-year civil engineering students a class in hydrology and water resources under the Faculty of Engineering
➢ Prepared, administered, and graded tests, assignments, and exams to assess the learning progress of the students

Mentor Jun - Jul 2012
Summer Engineering Experience for Kids (SEEK), NSBE, New Orleans, LA
➢ Taught Engineering principles to 3rd-8th graders to pique their interest in STEM (Science, Technology, Engineering, and Math)
➢ Designed various engineering projects with the students and prepared them for inter-class competitions

PROFESSIONAL EXPERIENCE

Consultant Aug 2015 - Dec 2016
Assorted assignments, Kampala, Uganda
➢ Worked with Proess Ltd., a consulting firm, on a resettlement action plan to assist in the relocation and compensation of people that would be affected by the
implementation of the proposed Kikagati Hydropower Project in southwestern Uganda
➢ Worked with a Professional Engineer on a number of assignments for the Ministry of Water and Environment, including writing proposals and inception reports to execute various water resources projects around the country

Site Engineer
Zzimwe Construction Company, Kampala/Kaabong, Uganda
➢ Supervised construction of one of the roads funded by the European Union under the Karamoja Roads Development Program
➢ Ensured that works were executed in accordance with the Bills of Quantities and specifications
➢ Organized site meetings to assess work progress with the Consulting Engineers
➢ Prepared weekly and monthly progress reports

INTERNSHIP EXPERIENCE

Student Trainee
Industrial Training with the Kampala City Engineer under the Makerere University Industrial Training Program
Project: Construction of the Oasis Shopping Mall, Yusuf Lule Rd, Kampala
➢ Learned various construction and construction management techniques on the site during the construction of the mall

Student Trainee
Industrial Training with the Directorate of Water Development (DWD) under the Makerere University Industrial Training Program
Project: Small Towns Water Supply and Sanitation Project (STWSSP), Mpigi, Uganda
➢ Learned various construction techniques during the construction of the offices for the STWSP in Mpigi town

PEER-REVIEWED PUBLICATIONS


CONFERENCE PRESENTATIONS AND AWARDS

NSBE Annual Convention – Pittsburgh, PA  
Poster and PowerPoint Presentations  
Title: Solar Powered Water Pumping System for Rural Underdeveloped African Communities, Case Study: Mbeere Community, Kenya  
Collaboration: Utah State University, UT, and RWTH Aachen University, Germany  
Award: 1st Place

NSBE Region 6 Fall Regional Conference – Tucson, AZ  
PowerPoint Presentation  
Title: Case Study Competition: Sustaining the Six–Energy Problem: System Optimization  
Goal: “To showcase the technical skills of the NSBE chapters in the region by applying their problem solving and analytical skills to real-life situations.”  
Award: 1st Place

OTHER AWARDS

➢ Graduate Research Assistantship (2010-2011; 2017-2021)  
➢ Graduate Student Senate Travel Award (Jan 2012)

PROFESSIONAL AFFILIATIONS

➢ National Society of Black Engineers (NSBE) 2010 - Present  
➢ American Society of Civil Engineers (ASCE) 2019 - Present

VOLUNTEER EXPERIENCE

Student Research Symposium, Research Week, USU  
Volunteered as a judge for the student research poster and PowerPoint presentations

NSBE, USU Chapter 2011 - 2014  
Organized students to participate in community outreach programs  
Mentored elementary school kids in STEM  
Participated in the Better World Books (BWB) book drive, collecting and donating textbooks from different colleges at the USU campus
➢ Set up and managed a booth sponsored by the USU school of graduate studies at NSBE conferences to talk to and encourage students from various universities around the country to pursue graduate studies at USU
➢ Partnered with the Society of Women Engineers (SWE) USU Chapter to organize the Evening with Industry Event (EWI) at the USU campus, where students get the opportunity to meet and talk to potential employers