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Controlling ammonia and sulfide inhibition during anaerobic digestion of slaughterhouse waste

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CONTROLLING AMMONIA AND SULFIDE INHIBITION DURING ANAEROBIC DIGESTION OF SLAUGHTERHOUSE WASTE

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A Thesis Submitted in Fulfilment of the Requirements for the Degree of Doctor of Philosophy in Materials Science and Engineering of the Nelson Mandela African Institution of Science and Technology

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ABSTRACT

The performance of experimental batch-reactor loaded with slaughterhouse waste at mesophilic temperature was investigated as well as the inhibition of both ammonia and sulfide in the aqueous phase during phase I of anaerobic digestion. The methylene blue method was used to quantify the amount of sulfide in the liquid phase whereby the amount of total ammonia nitrogen in the liquid phase was quantified by using Nessler method. The maximum CH_4 content of 69.6% was achieved at 0.37 VFA/Alkalinity ratio and pH of 7.51 during day 37 of anaerobic digestion. However, a sudden increase of ammonia nitrogen in the digester from day 44 to day 68 decreased the methane content by 62.15% from 65% to 24.6%. During phase II of anaerobic digestion, the efficacy of inorganic additives on the removal of total ammonia nitrogen and sulfide in the aqueous phase of slaughterhouse waste undergoing anaerobic digestion in the batch reactor was investigated for 65 days. A mixture of natural inorganic additives processed from the anthill and red rock soil samples collected from Arusha, Tanzania were used as adsorbents in different ratios. XRD analysis revealed that the anthill soil sample is endowed with quartz and hematite major mineral phases while red rock soil contains albite, pyroxene, and quartz as predominant phases. The anthill and red rock soil samples calcined at 900 °C displayed higher BET surface areas of 815. 35 and 852.35 m^2/g, respectively. Among all the adsorbent ratios investigated at different calcination temperatures, the ratio of 1:1 and calcination temperature of 700°C produced the highest adsorption capacities of both TAN and sulfide. Adsorption isotherm studies revealed that Jovanovich model fitted better to the experimental data than Langmuir and Freundlich models. The findings of this study have demonstrated that anthill and red rock soils can be exploited as affordable, ecofriendly and efficient adsorbents for mitigation of TAN and sulfide from the liquid phase and sustenance of methanogenesis.

DECLARATION

I, Eric Mutegoa do hereby declare to the Senate of the Nelson Mandela African Institution of Science and Technology that this thesis is my own original work and that it has neither been submitted nor being concurrently submitted for degree award in any other Institution.

Eric Mutegoa

Name and Signature of the Candidate Date

The above declaration is confirmed

Prof. Karoli N. Njau

Name and Signature of Main Supervisor Date

Prof. Askwar Hilonga

Name and Signature of Co-Supervisor Date

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CERTIFICATION

This is to certify that this thesis titled “Controlling Ammonia and Sulfide Inhibition during Anaerobic Digestion of Slaughterhouse Waste” has been written by Eric Mutegoa under the supervision of Prof. Askwar Hilonga and Prof. Karoli N. Njau of the NM-AIST. I approve to the Senate of the NM-AIST that this thesis qualifies for an award of Degree of Doctor of Philosophy in Materials Science and Engineering.

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DEDICATION

This thesis is dedicated to my family for nursing me with affections and love and their dedicated partnership for success in my life.

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LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviation/Symbol	**Description**
AC	Activated Carbon
AD	Anaerobic Digestion
AH	Anthill
BBC	Biobubble Column
BET	Brunauer-Emmet-Teller
BJH	Barret-Joyner-Hallenda
BOD	Biological Oxygen Demand
BTF	Biotricklling Filter
C/N	Carbon to Nitrogen
CEC	Cation Exchange Capacity
COD	Chemical Oxygen Demand
DIET	Direct Interspecies Electron Transfer
DO	Dissolved Oxygen
FE-SEM	Field Emission Scanning Electron Microscope
FT-IR	Fourier Transform Infra-Red
GHGs	Green House Gases
GST	Geological Survey of Tanzania
HFMC	Hollow Fiber Membrane Contactor
LCFA	Long Chain Fatty Acids
LOI	Loss On Ignition
MA	Mesoporous Alumina
MD	Membrane Distillation
MDCMD	Modified Direct Contact Membrane Distillation
MPA	Methane Producing Archaea
MSW	Municipal Solid Waste
NM-AIST	Nelson Mandela African Institution of Science and Technology
OTR	Oxygen Transfer Rate
OUR	Oxygen Utilization Rate

RPB	Rotating Packed Beds
RR	Red Rock
S/N	Sulfide to Nitrate
SGMD	Sweep Gas Membrane Distillation
SRB	Sulfur Reducing Bacteria
TAN	Total Ammonia Nitrogen
TKN	Total Kjeldahl Nitrogen
TS	Total Solids
VFA	Volatile Fatty Acids
VMD	Vacuum Membrane Distillation
VS	Volatile Solids
VWR	Van Waters and Rogers
WAS	Waste Activated Sludge
XRD	X-ray Diffraction
XRF	X-Ray Fluorescence Analyzer

CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

The world's dependence on fossil fuels as the main source of energy has triggered the evolution of new innovations in science and technology by researching on other simple and most affordable sources of energy (Afazeli *et al.*, 2014). This is due to the fact that the depletion of fossil fuels is imminent, but also the ecosystem has been endangered whenever these fossil fuels are burnt to release energy which is accompanied with unfriendly gases released to the atmosphere and subjecting the whole ecosystem to pollution (Shen *et al.*, 2013). One of the solutions is anaerobic digestion (AD) process through which biogas is generated when organic matter is degraded in the absence of oxygen (anaerobic digestion) (Jena *et al.*, 2017). Through biological and thermo-chemical routes, the biogas production process is considered as an alternative to fossil fuels and most affordable technology for energy production as a means of conserving the environment (Chandra *et al.*, 2012). The biogas technology has gained extreme importance recently since it can produce an alternative source of energy through the biological treatment of organic wastes with different characteristics (Yenigün & Demirel, 2013).

Anaerobic digestion is the process in which substrates with high organic content are treated in the absence of oxygen to produce biogas (Zhang *et al.*, 2016). Generally, biogas is a mixture of methane content (50 – 70%) and carbondioxide with other trace compounds such as ammonia, hydrogen sulphide and siloxane (Kougias & Angelidaki, 2018). The use of biogas becomes an environmentally friendly technology since it can be among the technologies to eradicate the emission of greenhouse gases (GHGs) through combustion process in which the carbondioxide released is less detrimental to the environment than biogas (Bharathiraja *et al.*, 2018). In practice, anaerobic digestion has been used to produce biogas in absence of oxygen from various organic wastes due to their availability and higher Carbon to Nitrogen ratio (C/N), but also as a means of waste management (Kim *et al.*, 2017). Both domestic and industrial activities have been the major source of tones of organic waste exposed to the environment in which biogas technology can be considered as the best solution to overcome their effect on the environment (Ma *et al.*, 2017).

The higher Carbon to Nitrogen ratio (C/N) ensures the sustainability of microorganisms and a proper balance of nutrient ratio between carbon and nitrogen in which high carbon content favours the maximum production of methane gas (Wang *et al.*, 2015), while nitrogen ensures nutrient balance for the growth of microorganisms. For example, more than 50% of total meat consumption in Tanzania is from beef cattle which accumulates a lot of waste during meat processing (Bwatota *et al.*, 2018). This situation portrays a need to utilize the particular waste as a means of resource recovery and waste management.

In this manner, different organic wastes such as cow dung (Alfa *et al.*, 2014; R. Li *et al.*, 2014; Zhou *et al.*, 2012), pig slurry (Abubaker *et al.*, 2015; Lallai *et al.*, 2002), slaughterhouse waste (Alvarez & Liden, 2008; Moukazis *et al.*, 2018; Salminen & Rintala, 2002), tannery wastewaters (Zupančič & Jemec, 2010), industrial effluents (Connaughton *et al.*, 2006; Yadav *et al.*, 2016), agro waste (Zahan *et al.*, 2018) and domestic wastes (Banks *et al.*, 2011; Cheerawit *et al.*, 2012) can be treated as potential substrates to initiate the anaerobic digestion (AD) process due to the higher ratio of carbon content present in such substrates. Generally, slaughterhouse waste is characterized by high organic content mainly composed of animal fats and protein components of blood (Alvarez & Liden, 2008; Ware & Power, 2016). Apart from numerous desulfurization reactions which catabolize cysteine to release sulfur in a reduced oxidation state, further degradation of this animal protein also releases both sulfur and ammonia into the aqueous environment which are regarded as inhibitory to the methanogens responsible for the methanogenesis process which is vital stage for producing methane during AD process (Lauterböck *et al.*, 2014). Besides the high carbon and organic content of the slaughterhouse waste, large amount of waste from meat industries is also produced which need to be regulated for protecting the environment against the spread of Bovine Spongiform Encephalopathy (BSE) (Bayr *et al.*, 2012), a common disease that affects cattle. In Tanzania, a lot of waste is also produced daily from meat industries since beef cattle accounts for more than 50% of the meat produced for human consumption (Bwatota *et al.*, 2018). Therefore, anaerobic digestion of slaughterhouse waste can be regarded as a cost effective solution to lower the environmental effects posed out by the waste and also producing biogas which can serve as energy source for domestic use.

Nevertheless, the stability of the digester's performance is highly affected by changes of parameters which may lead to inhibition and process failure. For instance, Hansen *et al.* (1999) showed that in a combined presence of both gaseous ammonia $(NH_3)_{(g)}$ and hydrogen sulfide

(H_2S) at lower concentrations, there is a high inhibition which affects the methanogenesis process.

The purpose of this study was to investigate among the two inhibitors, which one exceeds the recommended concentration in the liquid phase leading to inhibition process between sulfide (S^{2-})$_{(aq)}$ and dissolved ammonia (NH_3)$_{(aq)}$. During phase I of the AD process, the inhibition was evaluated by monitoring the reactor's performance at mesophilic temperature using the slaughterhouse waste as a substrate for AD process. The evaluation was done using parameters like pH, volatile fatty acids (VFA), alkalinity, ammonia-Nitrogen, sulfide and methane content produced.

However, batch reactors loaded with slaughterhouse waste were set for phase 2 experiment during this study. The selection of the substrate was based on its high composition of proteins and lipids mixed with water content (Rodríguez-Abalde *et al.,* 2017). For that case, slaughterhouse waste is regarded as a potential substrate for methane production during AD process. Meanwhile, during (AD), the breaking down of substrates rich in carbon content by microorganisms is sometimes associated with emission of unwanted contaminants in the digester which are considered as toxic to microorganisms. The excess production of other intermediate products such as siloxanes, halogens, ammonia, aromatics, hydrogen sulfide and volatile organic compounds can result into digester failure due to inhibition process which particularly affects methanogens (Córdova *et al.,* 2018; Mutegoa *et al.,* 2020). Since slaughterhouse waste is composed of animal fats and protein components of blood, the digestion process breaks down both cysteine + methionine amino acids which results into formation of sulfur (Bin *et al.,* 2017). Therefore, free ammonia is also accumulated in the aqueous phase because of high nitrogen content due to protein decomposition and long-chain fatty acids (LCFA) as a result of fat degradation (Wang *et al.,* 2016). The presence of both sulfur and ammonia in the liquid phase becomes inhibitory to methanogens during AD process, and as a result, the quality of biogas produced decreases. The inhibition occurs as a result of competition between sulfur-reducing bacteria (SRB) and methane-producing archaea (MPA) by oxidizing molecular hydrogen at high COD value (Huang *et al.,* 2020). It is reported that total ammonia nitrogen (TAN) in the range of 1500 – 5000 mg/L is inhibitory to microorganisms during biological treatments (Ding & Sartaj, 2016). Nonetheless, the concentration of ammonia nitrogen (NH_3 – N) above 2 mg/L can be toxic to aquatic species at a certain range of pH, temperature and other parameters (Al-Sheikh *et al.*, 2020). Subsequently, total sulfide ($HS^- + H_2S$) in the range of 100 – 800 mg/L is also reported as inhibitory to methanogens as it suppresses methane production (Sürmeli *et al.,* 2019). Several approaches such as ion exchange, struvite precipitation, membrane distillation, adsorption additives and C/N adjustment methods have been applied to lower various contaminants, dissolved ammonia inclusive in the liquid phase during AD process (Mutegoa *et al.,* 2020). Nevertheless, the mitigation process of dissolved ammonia and sulfide inhibition in the liquid phase can be grouped into two major groups namely; physical-chemical approaches and biotechnological method (Allegue *et al.,* 2012; Barbusiński & Kalemba, 2016). However, physical-chemical method which involves the use of various additives with high affinity to gaseous ammonia and sulfide had been dominating over other methods due to its high removal efficiency and affordability (Mrosso *et al.,* 2017). This method involves the adsorption process in which the surface of the adsorbent attracts gas molecules due to intermolecular forces. The process eventually results into a new chemical bond at the surface of the adsorbent as a result of chemical interaction between the surface of the material being adsorbed (adsorbate) and the adsorbent (Bergmann & Machado, 2015). Several adsorbents have been applied by researchers, for example, the use of zeolites through ion exchange for the removal of both forms of ammonia $(NH_3)_{(g)}$ and $(NH_4^+)_{(aq)}$, application of iron-rich materials such as iron pellets for hydrogen sulfide removal (Hina *et al.,* 2015; Janetaisong *et al.,* 2017). Furthermore, adsorption by activated carbon was reported to have a relatively low adsorption capacity of about 6.079 mg/g in removing dissolved ammonia from aqueous solution (Gotvajn *et al.,* 2009). Generally, most of the materials already existing are industrially synthesized which are readily expensive and unaffordable to apply for removal of contaminants in the liquid phase. It is therefore, recommended that economically feasible methods to be employed for lowering both ammonia and sulfide inhibition in order to elevate methane content produced during AD process.

In this study, cheaply and readily available inorganic materials rich in iron and aluminosilicate were collected, prepared and applied for both ammonia and sulfide removal in the liquid phase during AD of slaughterhouse waste. The selection of anthill soil and red rock soil was based on their elemental composition, such as iron in the form of magnetite (Fe_3O_4) and hematite (Fe_2O_3) (Janetaisong *et al.,* 2017). These iron contents are considered as remaining products of rocks that undergone leaching and oxidizing practices during the weathering process. The presence of iron oxide in the red soil is a major breakthrough for the precipitation of sulfide where hydrogen sulfide (H_2S) will be oxidized by the iron-based material into elemental sulfur

(Cristiano *et al.,* 2020). Meanwhile, the high amount of alumina (Al_2O_3) and silica (SiO_2) composing the aluminosilicate cage in anthill soil will provide a means of removing NH_3/NH_4^+ from the substrate undergoing AD process through ion exchange and adsorption processes (Šiljeg *et al.,* 2010).

1.2 Statement of the Problem

Protein-rich substrate, such as slaughterhouse waste, is a well-known source of sulfide and ammonia formation during anaerobic degradation. During anaerobic digestion of slaughterhouse sludge, large quantities of H_2S and dissolved ammonia $(NH_3)_{(aq)}$ may be produced in the biogas, causing many problems, such as inhibition of anaerobic digestion process, decrease of biogas production and methane content. The released dissolved ammonia $(NH_3)_{(aq)}$ from protein degradation is in equilibrium with the less harmful ionized ammonium species $(NH_4^+)_{(aq)}$. However, the non-ionized form of itself is also a source of inhibition of microorganisms, since the neutral gaseous ammonia $(NH_3)_{(g)}$ can easily pass through cell membranes of bacteria and archaea and upon entering the cell disrupts intra-cellular pH and concentrations of other ions.

Also sulfur in the liquid phase mainly exists in the form of organic sulfur, sulfate and sulfide. The H_2S can be derived from the hydrolysis of organic sulfur, the reduction of sulfates and the direct conversion of sulfides during anaerobic digestion. Sulfur in sludge has been considered as a key factor affecting the competition between sulfate-reducing bacteria and methane-producing bacteria, and sulfate reduction reaction increases with increasing the sulfur concentration. Therefore, methods to lower ammonia and hydrogen sulfide levels in anaerobic digesters treating high-protein substrates are desirable and subject to this study.

1.3 Rationale of the Study

Different studies on biogas production from different organic substrates have been done. The fate of both gaseous and dissolved ammonia and sulfide inhibition has shown that both quality and quantity of methane gas can be lowered, a condition which reduces the calorific value of methane gas. There have been several ways to purify the harvested methane gas. Still, these methods are not convenient since they lower the calorific value and general performance of methane gas during the purification process. This study provides a means of mitigating the inhibition process in the liquid phase during the primary stages of anaerobic digestion without affecting the quality and quantity of methane gas produced.

1.4 Research Objectives

1.4.1 General Objective

To develop powder-based materials for controlling ammonia and sulfide inhibition during anaerobic digestion of substrates rich in ammonia and sulfide.

1.4.2 Specific Objectives

(i) To determine the level of ammonia and sulfide in the liquid phase during anaerobic digestion of slaughterhouse waste operating at mesophilic temperature range.

(ii) To evaluate the capacity of selected natural inorganic additives in removing ammonia and sulfide in the liquid phase during anaerobic digestion of slaughterhouse waste.

(iii) To examine the effect of natural inorganic additives on the methanogenesis process.

1.5 Research Questions

(i) At what levels of ammonia and sulfide is the inhibition process induced during anaerobic digestion of slaughterhouse waste?

(ii) What is the capacity of natural inorganic additives in removing TAN and sulfide from the liquid phase during anaerobic digestion of slaughterhouse waste?

(iii) How do the inorganic additives affect the methanogenesis process?

1.6 Significance of the Study

This study is revealing the way the digester can operate in the appropriate range where the inhibition process is controlled when natural inorganic additives are employed as an affordable adsorbent materials. The study describes how much of the process stability in anaerobic digestion of slaughterhouse waste relates to the plant operation, which allows the microbiological consortia to adapt to the substrate with positive effects on the process, including energy savings, buffer level maintenance, better odor control, increased methanogenesis rate and higher biogas production with a well maintained process stability.

1.7 Delineation of the Study

In this study, cheaply and readily available inorganic materials rich in iron and aluminosilicate were collected, prepared and applied for both ammonia and sulfide removal in the liquid phase during AD of slaughterhouse waste. The purpose was to develop powder-based materials for controlling ammomia and sulfide inhibition during anaerobic digestion of substrates rich in ammonia and sulfide. The study also involved the description on how much of the process stability in anaerobic digestion of slaughterhouse waste relates to the plant operation, which allows the microbiological consortia to adapt to the substrate with positive effects on the process, including energy savings, buffer level maintenance, better odor control, increased methanogenesis rate and higher biogas production with a well maintained process stability.

CHAPTER TWO

LITERATURE REVIEW

2.1 Nitrogen-Rich Substrates

Microorganisms present in the reaction undergoing anaerobic digestion requires a balanced ratio of fermentable carbohydrate, nitrogen, phosphorous and other elemental nutrients for their normal growth (Ghasimi *et al.,* 2009). For instance, the research done in Salta, Argentina revealed that the organic fractions of C: N: P found in municipal solid waste (MSW) had an optimum ratio of 126: 7: 1 (Plaza *et al.,* 1996).

However, high nitrogen fractions in the substrate are not suitable as they result in an accumulation of ammonia during AD process. This phenomenon inhibits further growth of methanogens which lead to reduced biogas quality and quantity. Many literatures have reported a very high dissolved ammonia concentration in wastewater ranging from 1700 mg/L to 14 000 mg/L (Anjum *et al.,* 2017). In most cases, organic nitrogen in the digester can be presented as uric acids, amino acids and proteins, which is then hydrolysed to inorganic ammonia during the AD process. The released ammonia tends to accumulate during protein degradation, a process happening very slowly in the digester (Karthikeyan & Visvanathan, 2012). Substrates known to have high nitrogen contents are animal wastes, municipal wastes (bio-wastes), meat processing wastes and dairy wastes. Besides, being an inhibitor in the AD process, gaseous ammonia is also an environmental pollutant. Dissolved ammonia and the increased eutrophication, respectively, is noxious for fish species, it lowers the dissolved oxygen, highly corrosive and elevating infections (Lauterböck *et al.,* 2012). Many possibilities to control ammonia inhibition have been studied and reported in the literature. Some methods were practical and applicable in large scales, while some are still in research at lab-scale. However, each method has its pros and cons, depending on the inoculum, type, and characteristics of the substrate, reactor configuration, environmental and operational conditions.

2.2 Mechanism of Ammonia Inhibition

During AD process, a small amount of the organic nitrogen is biologically broken down to inorganic ammonia (NH_4^+–N/NH_3–N). Gallert and Winter (1997), reported that only about 1/3 and 1/2 of the total Kjeldahl nitrogen was converted to ammonia during mesophilic and thermophilic degradation. In the liquid phase, total ammonia occurs in two principal forms: the ionised form of the ammonia ion $(NH_4^+)_{(aq)}$ and the dissolved, unionised form of ammonia $(NH_3)_{(aq)}$. The dissociation equilibrium of ammonia in aqueous solutions (Equation (1) depends on pH and temperature. With a rise in pH and temperature the equilibrium shifts to aqueous ammonia $(NH_3)_{(aq)}$.

$$\mathrm{NH}^{+}_{4\,(aq)} \leftrightarrow \mathrm{NH}_{3(aq)} + \mathrm{H}^{+}{}_{(aq)} \tag{1}$$

The dissolved ammonia $(NH_3)_{(aq)}$ is in equilibrium with ammonium species $(NH_4^+)_{(aq)}$. The dissolved ammonia $(NH_3)_{(aq)}$, which is toxic with high permeability to the cell membrane of bacteria and archaea, can affect the intracellular pH, and concentrations of ions once entered the cell. Among the anaerobic degrading microorganisms, methanogens (Euryarchaeota) are reported to be the most affected groups by elevated dissolved ammonia levels (>1800 mg/L) and the first to be inhibited (Krakat *et al.,* 2017). However, the toxicity of dissolved ammonia which can be tolerated by microorganisms described in literature differed significantly, with concentration ranging between 50 to 1500 mg NH_3–N /L (Bujoczek *et al.,* 2000; Hansen *et al.,* 1998; Siles *et al.,* 2010).

2.3 Strategies to Overcome Ammonia Inhibition during Anaerobic Digestion Process

Recently, there have been several methods to reduce volatile ammonia which include the reduction of pH in which ammonium species $(NH_4^+)_{(aq)}$ is highly favoured over dissolved ammonia $(NH_3)_{(aq)}$ during the process, application of chemical additives is employed to adsorb nitrogen species. However, the use of physical covers, biofilters and scrubbers can also be employed for ammonia removal (Ndegwa *et al.,* 2008). Breakpoint chlorination and membrane-based technologies have been less commonly used, unlike some studies based on the alteration of substrate C/N ratios to ensure optimal microbial growth (Karthikeyan & Visvanathan, 2012; Kayhanian, 1999; Siles *et al.,* 2010). Meanwhile, stripping and chemical precipitation which are physical-chemical processes based have also been in use for mitigation of ammonia. However, also, the reduction of ammonia can either be done through a pretreatment step, during AD or as a post-treatment of the AD effluent (Serna-Maza *et al.,* 2015).

The ongoing depletion of fossil fuels on earth has influenced the significance of utilizing organic waste with a low-cost process treatment to harvest biogas as renewable energy (Beyene *et al.,* 2018; Khalil *et al.,* 2019). In turn, this technology has triggered the desire to increase the performance and efficiency of the process. Through the process, various studies have been done to remedy the effect of ammonia inhibition. This study highlights some of the strategies which have been recently in use to lower ammonia, and they have been categorized into three groups namely; optimization of substrate parameters and properties, physical-chemical processes and application of various additives.

2.3.1 Optimization of Substrate Parameters and Properties

The performance of the digester can be improved through optimisation of some parameters which can provide a conducive environment for microorganisms that are vulnerable to the unstable system of the reactor. In this case, ammonia inhibition can be reduced through optimisation of different properties and parameters following the substrate nature. For example, alteration of the C/N ratio, pH and temperature can be among the fundamental strategies to lower the ammonia inhibition level.

(i) pH and Temperature Adjustment

pH and temperature have been among the critical parameters which can be optimised to control the accumulation of ammonia in the digester during AD of wastewater (Wang *et al.*, 2012). The effect of pH and temperature increase does not only retard the growth of methanogens but also affects the production rate of biogas during anaerobic digestion (Xie *et al.*, 2015). For example, at pH range of 7.3 – 7.7 and TAN concentration of 2000 $mgNL^{-1}$, it was observed that both dissolved ammonia $(NH_3)_{(aq)}$ and ammonium species $(NH_4^+)_{(aq)}$ induces the inhibition process largely as per both experimental and model results (Astals *et al.*, 2018). Generally, during the thermophilic condition in which the operating temperature is above 40 °C, there is an accumulation of fatty acids which inhibits the growth of methanogens resulting into low biogas production (Jena *et al.*, 2017). Different studies have suggested that there is a relationship between the biogas produced during the AD process with a range of temperature settings. These results revealed that there is a linear correlation between the biogas produced with temperature from 25 °C to 44 °C. Although higher temperature (thermophilic) influences rapid degradation of substrates, it is not recommended due to its little effect on biogas production rate, large energy input and operational complications, hence not economically feasible (Chae *et al.*, 2008).

However, the variation of pH and temperature can influence the transition of ammonium ion $(NH_4^+)_{(aq)}$ and dissolved ammonia $(NH_3)_{(aq)}$ in the liquid phase (Zhang *et al.,* 2005). Thus, this phenomenon is very crucial in determining the equilibrium shift between the two species since NH_4^+ is not toxic to methanogens and is regarded as a potential fertiliser (Hunt & Boyd, 1981). Furthermore, it is indicated from other researchers that biogas production can be reduced when there is an increase in temperature due to the dissolved ammonia $(NH_3)_{(aq)}$ released in the reactor, which ultimately inhibits the methanogenesis process (Angelidaki & Ahring, 1994; Hansen *et al.,* 1999).

Therefore, it is recommended that in order to lower ammonia inhibition during AD of the substrate rich in nitrogen compounds, the digester should be operated at a pH that ranges between 7.2 and 8, and configured at mesophilic condition (Siegrist *et al.,* 2002).

(ii) Changing the Carbon/Nitrogen Ratio

The carbon to nitrogen ratio is another important parameter which can determine the feasibility of microorganisms during the AD process (Kumar *et al.,* 2010). Since carbon is used for energy production and nitrogen being used for building cell structure, a combination of the two elements is a paramount factor determining the survival of microorganisms during the AD process. To ensure the sustainability of microorganisms in the reactor undergoing AD process, there is a need to balance the nutrients supplied from both carbon and nitrogen in the ratio which the amount of carbon is higher than nitrogen. For example, Dai *et al.* (2016) reported that the adjustment of C/N ratio to 17/1 during AD of waste activated sludge (WAS) and perennial ryegrass co-digestion enhanced high production of methane content in the biogas. However, from the study done by Xu *et al.* (2016), it was observed that heterotrophic bacteria in the AD system were actively playing a major role in removing ammonia when the C/N ratio was higher than 18/1. If the amount of nitrogen exceeds that of carbon (low C/N ratio), the excess amount of nitrogen is converted to ammonia which becomes inhibitory for methanogens (Astals *et al.,* 2012; Mata-Alvarez *et al.,* 2011; Wang *et al.,* 2012).

It is vital to control the C/N ratio during the AD process to reduce the possibility of ammonia accumulation in the digester when the nitrogen content exceeds carbon (Dai *et al.,* 2016). Co-digestion is among of the appropriate solution to get a better carbon to nitrogen balance in which different organic materials are mixed to enhance the stability of AD process (El-Mashad & Zhang, 2010; Mshandete *et al.,* 2004). However, there are other several benefits which can be obtained through co-digestion process. Some of the benefits include the dilution of the potentially toxic compounds, both pH and moisture contents are adjusted, and the buffer capacity to the mixture content is maintained (Esposito *et al.,* 2012).

Therefore, the inhibitory effect of ammonia can be alleviated through anaerobic co-digestion of different organic substrates provided that the C/N ratio ranging between 15 and 30 is obtained. This ratio is usually regarded as the optimum ratio after mixing the substrates and is considered to be perfect for a stable AD process (Li *et al.,* 2009; Zhang *et al.,* 2013).

2.3.2 Physical-Chemical Processes

Most of the protein-rich substrates are composed of nitrogen fragments and carbon, which determines the sequence of amino acids which are regarded as building blocks of protein. The excess of nitrogen fragments in the digester can form various forms of nitrogen groups such as NH_3, NH_4^+ and NH_3–N, which induces the inhibitory effect to methanogens in the reactor (Chiu *et al.,* 2007). However, dissolved ammonia effect in the anaerobic digester can be removed by physical-chemical processes such as air ammonia stripping, the formation of struvite and membrane filtration (Guštin & Marinšek-Logar, 2011).

(i) Air Stripping

Air stripping is the technology which separates the volatile organics from wastewater by rising the surface area of wastewater exposed to air. The method involves the mass transfer of volatile contaminants from water to air (Gorre & Himabindu, 2014). This method is sometimes accompanied by direct aeration treatment which forces the air through a reactor; as a result, the volatile ammonia is released to the atmosphere. Recent studies show that both CO_2 and biogas produced during the AD process can be used for stripping process because of their potentiality in adjusting the pH of the anaerobic digestion effluent (Laureni *et al.,* 2013; Lei *et al.,* 2007).

For example, Liao and other co-authors, Liao *et al.* (1995), from their study revealed that during the stripping method, there are three factors to take into consideration when removing ammonia in both forms, either as ammonium ion or volatile ammonia. These factors are temperature, pH and the ratio of air to wastewater flow rate. The method further revealed that the volatility of ammonia depends on temperature whereby the air temperatures must be upheld at appropriately steep levels. For example, Georgiou *et al.* (2019), in their findings, concluded that the temperature above 45 °C is mostly favoured for air stripping. Moreover, when ammonia removal was considered for ammonia fermented swine manure, the efficiency was 90% and 85% for air stripped at pH of 8.8 and 10.2, respectively (Huang *et al.*, 2019). However, the decrease in ammonia removal efficiency from 90% to 85% was due to the increase of pH from 8.8 to 10.2, which was adjusted with the addition of lime before the stripping process. Lime addition such as calcium hydroxide ($Ca(OH)_2$) is usually done in order to elevate the pH for simplifying the volatilization of ammonia and removal of heavy metals through co-precipitation of other organic macromolecules and particulate matters present in the substrate (Renou *et al.,* 2009). Among of the drawbacks of this method is the packed tower in which results into the formation of suspension due to solid particles which are a result of slaked lime added in the wastewater for pH adjustment (Quan *et al.,* 2009). However, Yuan *et al.* (2016) revealed that high mass transfer performance could be achieved when rotating packed beds (RPB) are used to enhance a continuous flow compared with packed towers which demand the stripping tanks. Generally, RPB's are very small in size, which improves the high efficiency and short retention time.

Table 1: Tower air-stripping experiments

Experiment No.	T. S (%)	NH_3-N (mg/l)	Air Flow (l/min)	Liquid Flow(l/min)	Air/liquid (ratio)	pH	T°C
1	0.659	1951	45	0.830	54.2	9.4	22-25
2	0.663	2192	45	0.861	52.3	11.5	22-24
3	0.942	2154	65	0.877	74.1	10.6	21-23
4	0.942	2142	65	0.833	78.0	9.5	21-23
5	0.942	2072	65	0.870	74.7	11.9	21-22
6	1.953	838	65	1.172	55.5	10.6	21-22
7	1.953	819	90	1.171	76.9	11.5	19-23
8	2.963	706	90	1.062	84.7	10.6	16-19
9	2.963	694	90	1.034	87.0	9.6	17-22
10	0.649	2152	90	0.883	101.9	11.7	13-18
11	0.613	2192	90	0.863	104.3	9.4	6-14
12	0.613	2192	90	0.870	103.4	10.6	8-15
13	0.651	1812	90	0.851	105.8	10.7	18-21
14	0.651	2031	90	0.845	106.5	11.7	18-21

Liao *et al.* (1995)

pH Effects

Results from the experiment which was done by Liao *et al.* (1995) (Table 1), indicates that ammonia removal in swine wastewater was achieved at 90.3% removal efficiency, 22 °C, pH of 9.5 and airflow rate of 45 L/min for 55 hrs. However, the higher removal efficiency was achieved as the pH decreased below 10 while increasing the pH above 10 was not significantly inducing the ammonia removal efficiency. Through mass transfer, the stripping process is enhanced by elevating the pH, favouring the transition in the chemical equilibrium between dissolved ammonia $(NH_3)_{(aq)}$ and ammonium species $(NH_4^+)_{(aq)}$ (equation 1). This phenomenon suggests that the pH should be maintained in alkaline media in which the equilibrium shift lies in the direction of dissolved ammonia as it would be substantial for increased ammonia removal efficiency during the recovery process (Ferraz *et al.,* 2013).

The Effects of Airflow Rate

The stripping technique was aided by rising the airflow ratio from 52 to 73 regardless of the pH change. However, the stripping efficiency increases when the airflow rate was kept constant at 65 L/min but this increase did not influence the ammonia removal efficiency since the removal efficiency remained the same when the flow tare was enlarged to 90 L/min. Consequently, when the airflow rate increases also the liquid – surface area increases which make the amount of gaseous ammonia $(NH_3)_{(g)}$ diffused in air to be easily controlled (Srinath & Loehr, 1974). Nevertheless, it is recommended that the optimum airflow rate be 5L/min for 1L of wastewater because the increase in airflow rate influences a high demand of engineering operational cost with little increase in ammonia removal efficiency (Lei *et al.,* 2007).

Temperature Effects

The liquid and air temperatures are the factors which seem to be influencing the ammonia removal efficiency at the pH below 10.5 as described elsewhere. Nevertheless, the ammonia removal efficiency was not significant above pH 10.5 as the temperature was increasing (Campos *et al.,* 2013). From these observations of temperature influence, it was recommended that ammonia stripping processes should be done during warm weather (Liao *et al.,* 1995).

From the study of Bonmatı and Flotats (2003), it was observed that a combination of air stripping and absorption could be applied to eliminate and restore ammonia from pig slurry whereby sulfuric acid was used to absorb ammonia transferred in the air from waste. The experiment was done basing on pH and temperature as the factors in assessing the feasibility of the process and found that an initial pH of 11.5 was significant for removing ammonia regardless of the temperature which was increased up to 80° C.

Since ammonia stripping method involves the transition of ammonium ion $(NH_4^+)_{(aq)}$ and gaseous ammonia $(NH_3)_{(g)}$ in the liquid phase (Deublein & Steinhauser, 2011), the shift of the equilibrium towards ammonia gas $(NH_3)_{(g)}$ (Lei *et al.*, 2007) can be achieved through variations of the two parameters, pH and temperature of the medium. The coexistence of both ammonium and ammonia species in the liquid phase can be described in the equation below:

$$[NH_3] = \frac{[NH_3 + NH_4^+]}{1 + [H^+]/k_a} \tag{2}$$

For instance, Guštin and Marinšek-Logar (2011), examined the pH and temperature parameters for the feasibility of the biogas plant operating conditions. The findings of ammonium exclusion were correlated with tentatively determined values of gaseous ammonia at the same conditions. Through the stripping method, ammonium ions were removed by 92% whereby total nitrogen from the anaerobic effluent was also removed by 88.3%. It was observed that the high pH was profoundly influencing the stripping process, favouring the change in ammonia/ammonium ratio over gaseous ammonia. Moreover, the quantity of air which was outflowing through the stripping bench impacted the conversion of ammonia from the liquid phase to the gaseous phase with little effect of the temperature.

For this case, air stripping seems to be a convenient method for the wastewater treatment process, particularly in the recovery of valuable ammonia and other nitrogen species. To maximise the efficiency of the process, air stripping must be operated in a packed tower for providing a large mass transfer area (Djebbar & Narbaitz, 1998).

Ammonia Recovery Process

Since ammonia gas is released to the environment during the stripping process, there should be a mechanism to prevent the direct release of the ammonia gas to the environment as it can affect the ecosystem due to its toxicity. Many kinds of literature consider ammonia stripping process coupled with absorption as an alternative method for ammonia removal in the final stage of the process (Bonmatı & Flotats, 2003). In most cases, sulfuric acid (H_2SO_4) is used as an absorbent in which gaseous ammonia $(NH_3)_{(g)}$ reacts with $H_2SO_{4\,(aq)}$ forming ammonia salt $(NH_4)_2SO_{4\,(s)}$ that can be used as a fertiliser (Lei *et al.*, 2007).

(ii) Struvite Precipitation Method

Struvite precipitation is among of persistent efforts made so far to lessen the loss of ammonia in the composting operation by generating the struvite crystallisation in the compost mixed with the addition of water-soluble Mg and P salts (Huang *et al.*, 2014). The gaseous loss of ammonia was lowered by the growth of struvite crystals which influenced a massive increase of ammonia content in the compost up to 1.5%. The other findings by Jeong and Hwang (2005), tried to scrutinise how the aggregation of ammonia could change the overall behaviour of nitrogenous materials into struvite crystals.

This approach has been applied to numerous wastewaters, including swine waste (Burns *et al.,* 2001; Nelson *et al.,* 2003), agro-industrial effluents (Altinbas *et al.,* 2002), landfill leachate (Altinbaş *et al.,* 2002; Li *et al.,* 1999), calf manure (Schuiling & Andrade, 1999), coke manufacturing (Zdybiewska & Kula, 1991), leather tanning (Tünay *et al.*, 1997) and anaerobic digester sidestreams (Battistoni *et al.,* 1997; Fujimoto *et al.,* 1991). The removal of (NH_4^+), phosphate (PO_4^{3-}) or both from wastewater by struvite precipitation is usually done by the addition of Mg^{2+} ion, which is specifically meant for changing the solubility product equilibrium and triggering precipitation. Different sources of Mg^{2+} ion, for example, $Mg(OH)_2$, MgO, $MgCl_26H_2O$, etc., have been in use for ammonia removal by struvite precipitation (Uludag-Demirer *et al.,* 2005).

Formation of Struvite

According to Kim *et al.* (2007), the equation below shows how white crystalline solid of struvite forms:

$$Mg^{2+}{}_{(s)} + NH_4^+{}_{(aq)} + PO_4^{3-}{}_{(aq)} + \longrightarrow 6H_2O_{(aq)}\ MgNH_4PO_4 .\ 6H_2O_{(s)} \qquad (3)$$

The formation of struvite in a solution is a pH-based reaction because the precipitating ions are all pH-dependent.

Subsequently, struvite precipitation is primarily based on the thermodynamic equilibrium of constituent ions in the solution. Kim *et al.* (2007) conducted a study in which the feeding of chemicals such as magnesium, orthophosphate and buffering reagent were studied to affirm the performance variation of struvite precipitation rendering to the feeding sequence. In this study, magnesium chloride and potassium phosphate solutions were used at different concentrations in the molar ratio of Mg: PO_4 1: 1.2: 1.2 for NH_4^+–N removal (Ohlinger *et al.,* 1998). The NH_4^+–N removal capability was found to be less than 50% as a result of the high accumulation of PO_4^{3-} and Mg^{2+} ions which eventually dropped the pH to 6. The decrease in pH affected the crystallisation and precipitation of the solution resulted from the dissolution of the struvite.

Furthermore, the efficiency in removing NH_4^+–N was increased to 78% when the pH was increased to 9.2 and decreased when the pH was increased above 9.4 (Ryu *et al.*, 2008). On the other hand, magnesium and orthophosphate dosage were examined and found that the molar ratio affected the removal efficiency in which the NH_4^+–N removal was greatly affected by the concentration of orthophosphate in the solution much more than that of magnesium ions (Escudero *et al.*, 2015).

It can be concluded that pH is also among important parameters to consider besides the dosage of orthophosphate and magnesium ions when this approach is applied.

(iii) Membrane Distillation Method

The membrane distillation (MD) method is a thermally determining operation in which a mixture across a hydrophobic microporous membrane is separated by physical means. The membrane operates as a boundary to isolate a heated solution from a more cooling chamber which encompasses either a liquid or a gas phase (Banat & Simandl, 1998). Recently, the technology has been used considerably for volatile compounds removal such as ammonia due to its hypothetically low energy prerequisite. It is most likely for recovering and reuse precisely, which can be an advantageous approach for wastewater treatment having a relatively low level of volatile compounds but operating under high temperature. The simulation experiment which was done by Xie *et al.* (2009), on wastewater encompassing low concentration of ammonia (100 mg/L) with sweep gas membrane distillation at pH 11.5 showed the ammonia removal was achieved by 97% at uppermost temperature and fastest gas flow. The feed rate and gas flow were also investigated in which from 59 to 100mL/min, the removal efficiency increased from 67 to 77% after two hours. The further increase of the feed rate from 100 to 250 mL/min had a trivial impact on the removal rate contrary to the feed temperature, which increased the ammonia removal rate. On the other hand, the increase in temperature (about 40 °C) influenced the diffusion of ammonia in the membrane pores due to higher mass transfer coefficient (Lin *et al.*, 2018). This phenomenon is regulated by the endothermic nature of the feed solution, which enables the volatility and dissociation of ammonium ions.

Nevertheless, the ammonia removal efficiency was investigated using a modified direct contact membrane distillation (MDCMD) in the aqueous solution, which was compared with the hollow fibre membrane contractor (HFMC). In line with this experimentation, the effect of controlling parameters such as pH, temperature and contact time were also examined in which the experimental results showed that the higher ammonia removal efficiency was 99.5% for MDCMD compared to 52% and 88% for DCMD and HMC within 105 min, respectively. The best feed pH of 12.20 was proved to be the main factor in the modified direct contact membrane distillation (MDCMD). The increase in feed temperature and flow rate influenced the higher ammonia mass transfer coefficient, ammonia removal efficiency and permeate flux within the examined range. Considering different MD configurations, the findings in 2013 and 2015 (Duong *et al.*, 2013; Fang *et al.*, 2015), focused on the application of sweep gas membrane distillation (SGMD) and vacuum membrane distillation (VMD) for eliminating the little amount of ammonia in the liquid phase. The study involved the investigation on the effects of feed flow rate, feed temperature, sweep gas flow rate and vacuum degree as operating parameters for ammonia removal and separation performance. The impact of different factors, such as the feed temperature, the feed flow rate, airflow rate and vacuum degree, inside the membrane module on ammonia overall mass transfer coefficient, ammonia flux and separation factor were examined.

Table 2: Effect of sweep gas flow rate and vacuum degree on overall ammonia mass transfer coefficient (Kov) at feed temperature of 65 °C and feed flow rate of 0.3 L/min

SGMD		VMD	
Sweep gas flow rate (L/min)	**K_{ov} (10^{-5} m/s)**	**Vacuum degree (torrs)**	**K_{ov} (10^{-5} m/s)**
0.4	0.86	300	1.00
2.0	2.02	200	2.25
3.0	2.58	130	5.58
5.0	3.21	100	10.97

Duong *et al.* (2013)

From Table 2, it is evident that the increase in sweep flow rate from 0.4 to 5.0 L/min, influenced the increase in overall mass transfer from 0.86×10^{-5} to 3.21×10^{-5}m/s. Meanwhile, the VMD had much dependence on pressure variations in the vacuum membrane in which as the pressure decreased from 300 to 100 torrs influenced the overall mass transfer increase 1.00×10^{-5} to 10.97×10^{-5} m/s. However, a related tendency was reported in earlier studies (Ding *et al.*, 2006; El-Bourawi *et al.*, 2007; Lawson & Lloyd, 1997). Apart from other factors such as feed rate, airflow rate, vacuum degree and feed temperature, which affects the separation process and mass transfer coefficients calculated (*Kov*), the results show that *Kov* for VMD is higher than that for SGMD when the process is treated at the same conditions. These results suggest that the ammonia removal efficiency was improved by increasing sweep gas flow rate or by decreasing downstream pressure.

2.3.3 Application of Various Additives to Lower Ammonia Inhibition Level

Various additives have been used to reduce the ammonia volatilization, predominantly, with acidifying and adsorbent additives. The acidifying additives have been potentially used to shift the equilibrium between dissolved ammonia $(NH_3)_{(aq)}$ and ammonium species $(NH_4^+)_{(aq)}$ in which the pH reduction favours the formation of more ammonium ion (NH_4^+) species in the equilibrium (Hansen *et al.,* 1998), which is less toxic to methanogens when compared to dissolved ammonia $(NH_3)\,)_{(aq)}$ species (Zhang *et al.,* 2014). In this study, the role of additives in removing ammonia has been categorized under ion exchange and adsorption methods.

(i) Ion Exchange Method

Ion-exchange is among several approaches that are commonly used in removing dissolved ammonia from the water. This process generally incorporates captivating species of interest (ammonia) through ion exchange and adsorption technique. These ion exchangers usually exist as either natural or artificial. In most cases, minerals that are crystalline, hydrated, aluminosilicate of alkali, or alkaline earth ions provides ion exchangers with high adsorption capacity (Adam *et al.*, 2018).

It is this condition which brings about the ion exchange process as an alternative method for ammonia removal, specifically the ammonium ion (NH_4^+) (Jorgensen & Weatherley, 2003; Romero-Güiza *et al.,* 2016). Ion exchangers are advantageous over biological treatment since their performance is not pH and temperature-dependent, conditions which are necessary for biological removal of ammonia. For this case, ion exchangers can still work in the presence of antimicrobial compounds (Jorgensen & Weatherley, 2006). Clinoptilolite and zeolites which occur naturally, are among several ion exchangers reported in the literature for effective ammonia removal from wastewater (Jorgensen & Weatherley, 2003). The equilibrium mechanism between the ion exchanger and ammonia is given below:

$$(M^- A^+)_{(s)} + (\text{Ammonium}^+)_{(aq)} \leftrightarrow (M^- \text{Ammonium}^+)_{(s)} + (A^+)_{(aq)} \text{ (Heisler et al., 2008)} \quad (4)$$

Jorgensen and Weatherley (2006), examined the performance of fixed beds of exchanger resin consisting of clinoptilolite (natural zeolite), Dowex50w-x8 (gel resin), and Purolite MN-500 (macronet resin) for comparison of ammonium ion removal efficiency. Secondly, the influence of two contaminants which are citric acid and whey protein isolate for ammonium ion breakthrough was determined. Thirdly, the breakthrough performance of the exchanger resin after regeneration was determined. Finally, the effect of the pollutants upon regeneration performance was examined and revealed that the occurrence of organic compounds had a varying impact on ammonium ion adsorption. In the case of clinoptilolite, it was found that the presence of protein seemed to have less effect upon ion exchange capacity. However, when the clinoptilolite was mixed with the MN-500, a significant improvement in the reduction of ammonium ion capacity was noticed in the presence of citric acid. Regardless of acetic acid being a weak acid, the effect of its presence on the ion exchanger signifies its role for competing with protons in the cationic sites on the exchanger. After cycles of exhaustion and regeneration, clinoptilolite was very superior over synthetic resins, which displayed a reliable performance in each run.

However, apart from resin, there are other materials which can be used for the ion exchange process in removing NH_4^+–N. For example, the work which was done by Liu and other co-authors in 2011 Liu *et al.* (2011), to test the ammonia removal efficiency by the calcinated kaolin, it showed that the extruded powder material of 1 - 2 mm grain size was superior for the ammonia removal process. Results indicated that ion exchange capacity, which was studied by Cation Exchange Capacity (CEC), was above the concentration of 70 mg NH_4^+–N /g for the material prepared. In wastewater treatment, 90% of the ammonia nitrogen could be removed using this material.

The other study involved the use of ion exchange materials for ammonia removal (Tao *et al.*, 2017) and assessing the effect of pH reduction on the of digesters’ performance, particularly the features of the microbial community. The extended removal of NH_4^+–N was completed over ion-exchanging at both temperatures (thermophilic and mesophilic), with ordinary removals of 50 and 70% for the clinoptilolite and resin dosed reactors, respectively. The pH reduction was approximately done at the unit of 0.2 – 0.5 dosages in the reactors which eventually decreased the dissolved ammonia concentration in the range between 600 and 90 mg/L at 43 °C. At these conditions, methane yield was increased by 54% due to alleviation of ammonia inhibition. Some criterions such as flow rates, and pH were examined (Wirthensohn *et al.*, 2009) to evaluate the ability of acidic gel cation exchange resins and clinoptilolite in column experiments to remove ammonium ion. It was found that the quality of the effluent was very reasonable (NH_4^+–N < 2 mg/L) and ammonium ion removal efficiency was nearly 99%.

Ammonia – ammonium equilibrium in the aqueous phase is principally pH-dependent (Hedström, 2001) whereby ion exchange can be used to remove the ionized form from a solution. The performance of MesoLite for ion exchange in the liquid phase was investigated (Thornton *et al.,* 2007). In this experiment, 100 ml of NH_4^+–N solution was used to equilibrate with 0.5 g of MesoLite grain size ranging from 0.1 – 0.6 mm. Different concentrations were varied when the sample of MesoLite was equilibrated with (0–2000 mg/l NH_4^+–N) at 20 °C for 24 h. Consequently, 15% of sodium silicate was added in the mixture as a binding agent which was mixed at the same proportion as the crushed sample. The effect of contact time on the equilibrium capacity based on kinetic experiments was studied at different intervals of (5, 10, 15, 30, 45, 60, 120, 180 and 240 min) to examine the adsorption properties of the material. Langmuir and Freundlich isotherm models fitted adequately with the results obtained as well as a better explanation of the mechanism. A maximum equilibrium capacity of 49 g NH_4^+–N kg^{-1} was obtained, indicating that the increase in solution concentration and contact time provided the best performance at an optimum pH between 6 and 7. Through this study, it was concluded that the capacity of the MesoLite material is greatly influenced by solution concentration and pH between 6 and 7.

(ii) Adsorption Method

The most preferred adsorbents are those with high surface area and small pores for efficient removal of contaminants. Ammonia adsorption using these porous materials has been progressively discussed for their applications (Furtado *et al.,* 2011; Helminen *et al.,* 2001; Johnson *et al.,* 2012). Recently, conventional inorganic adsorbents such as activated carbon, alumina, silica gel, and 13X zeolite, have been in use nevertheless their low adsorption capacities they exhibit in the range from 2.3 to 12.0 mol/kg (37 to 192 mg/g) (Helminen *et al.,* 2001). For adsorption purposes such as ammonia, the adsorbents must have a higher surface area with small pore sizes to enhance the chemical interaction between the surface of the adsorbent and the adsorbate. Several inorganic nanoporous materials have been in use as an alternative to zeolites and activated carbon for gaseous adsorption (Ruckart *et al.,* 2016). Activated carbon seems to be more advantageous over other porous solids due to its larger surface area, extremely established porous structure and the ability of the porous structure to be modified further for special applications (Marsh & Reinoso, 2006). Since the activated carbon generally consists of non-polar surfaces, both pre and post-synthesis treatment as a means of modifications are crucial when adsorbing polar gases (eg. NH_3). The removal of ammonia in wastewater using activated carbon is affected by many factors such as textural properties but also the chemical nature of its surface and nature of oxygen-containing functional groups (Faria *et al.,* 2004).

By considering the role of surface modification for proper adsorption of ammonia (Gonçalves *et al.,* 2011), the impact of functional groups in the exclusion of ammonia using an improved resin-based activated carbon was studied. The results indicated that the activated carbon, which was modified by nitric acid, had improved the adsorption capacity at room temperature. Supposedly, there is a correlation between the total adsorption capacity and the amount of supplementary acidic and fewer stable oxygen surface groups. Related researches show that there is a relationship between the humidity and surface chemistry of the carbon used in which the moisture enhances the adsorption capacity of the adsorbents due to the dissolution behaviour between ammonia and water. However, the presence of moisture at the surface of the carbon material has little effect on the adsorption process since both Brønsted and Lewis acid centres offer more adsorption pathways from the carbon surface. The formation of both NH_4^+ and NH_3 species were confirmed by FTIR analyses of the exhausted oxidised samples. The interaction between lone pair electron of NH_3 species with graphene layers through Lewis acid sites is in agreement with the conclusion that total surface area, interior porous structure and the existence of functional groups on the pore surface of activated carbon are very crucial for determining the adsorption capacity (Ahmedna *et al.,* 2000).

Meanwhile, Yeom and Kim (2017) did a study on inorganic nanoporous materials such as mesoporous alumina (MA) which were investigated to replace the role of zeolite and activated carbon for NH_3 adsorption. The characterization of MA showed uniform pore size distribution and interlinked pore system, properties which were superior over other commercial adsorbents (activated carbon, zeolite, and silica powder). The free hydroxyl groups in MA serves as useful adsorption locations for NH_3 connected with interlinked adsorbent pore system, which is an important feature to enhance adsorption.

In addition to that, the ammonia inhibition level was studied by investigating the appropriateness of a mixture of activated carbon and limestone in reducing ammoniacal nitrogen which was existing in a considerable quantity (between 429 and 1909 mg L^{-1}) in one of the disposal areas in Malaysia (Aziz *et al.,* 2004). It was observed that either activated carbon or a mixture of both activated carbon and limestone in a ratio of 5:35 could remove 40% of ammoniacal nitrogen present in a landfill. Therefore, from the study and results obtained, it can be concluded that limestone is theoretically suitable as a substitute material to replace activated carbon at an affordable cost.

Table 3: Summary of methods and their appropriate conditions for the operation of the AD system in controlling ammonia inhibition

Method/technique	Appropriate condition(s)	Reference
pH and temperature adjustment	-Alkaline pH range between 7.3 - 7.7. -Mesophilic temperature (35 ℃ - 45 ℃).	Astals *et al.* (2018), Mpofu *et al.* (2020), Wang *et al.* (2019), Zinatizadeh and Mirghorayshi (2019)
C/N ratio adjustment	-C/N ratio ranging between 15/1 and 30/1 is convenient for reducing ammonia inhibition.	Li *et al.* (2019) and Xu *et al.* (2016)
Air stripping	-Temperature above 45 ℃ for volatilisation of ammonia -pH range between 8.8 – 10.2 -High stripping tower to facilitate air temperature for volatilisation of ammonia.	Georgiou *et al.* (2019), Huang *et al.* (2019) and Li *et al.* (2020)
Struvite precipitation	-1.5% compost mixture of water-soluble Mg and P salts. -Molar ratio of 1.5:1:1.5 of Mg/N/P and pH of 9.5	Hu *et al.* (2020) and Huang *et al.* (2014)
Membrane distillation	-High feed temperature (≥40 ℃) and low downstream pressures influence diffusion of ammonia in the membrane pores. -Ammonia removal efficiency is increased as water pH is raised to 10.	He *et al.* (2018) and Lin *et al.* (2018)
Ion exchange	-Acidic medium for facilitating ion exchange through protons which competes with cationic sites. - Extruded powder materials of 1-2 mm grain size are superior for the ammonia removal process. -Optimum pH between 6 and 7.	Ham *et al.* (2018) and Thornton *et al.* (2007)
Adsorption	- High surface area and small pores for sufficient chemical interaction between the surface of the adsorbent and the adsorbate. -Adsorption capacity is favoured most at high adsorbent dosage. -pH range between 3 - 8	Al-Sheikh et al. (2020) and Huang *et al.* (2018)

2.4 Operating Conditions to Improve Ammonia Removal in the Anaerobic Digestion System

From the above explained strategies on how to remove ammonia in the substrates rich in nitrogen during the AD process, there are some parameters which play a vital role for the effective removal of ammonia during AD process. In fact, parameters such as pH level, amount of air, C/N ratio and temperature are considered to be economically viable operating conditions in a biogas reactor (Guštin & Marinšek-Logar, 2011). For example, when the pH is adjusted to alkaline level, it affects the stripping process in which the ratio of ammonia/ammonium is altered, favouring ammonia removal efficiency due to the equilibrium shift as shown in

Equation (1). However, ammonia removal efficiency may be improved by air passing through the stripping bench plant which compresses the ammonia in the liquid phase hence vaporize the dissolved ammonia which is then transformed to the gas phase (Georgiou *et al.*, 2019). Meanwhile, the C/N ratio is also among the important parameter to lower ammonia inhibition since when adjusted, it can favour the growth of microorganisms and maximize the production of methane. The C/N ratio may be increased by the addition of carbohydrate substrates into which the level from 20/1 to 30/1 is considered to be appropriate for metabolic activities of microorganisms and VFA production (Li *et al.,* 2019). Nevertheless, the temperature is also regarded as a potential operating condition during AD for ensuring process stability and overwhelming inhibition progression. It has been observed that setting the digester temperature above 40 ℃ (thermophilic condition), is not an effective way to improve the digestion process due to accumulation of excess fatty acids which in turn affects the growth of methanogens though high-temperature influences rapid degradation (Zinatizadeh & Mirghorayshi, 2019). In practice, for better performance of the digester during biogas production, it is recommended that mesophilic condition (30 ℃ - 40 ℃) should be adopted especially when treating agricultural organic waste for AD process (Wang *et al.,* 2019).

Table 4: Advantages and disadvantages of current methods for ammonia removal

Method	Advantages	Disadvantages	References
pH and temperature adjustment	The method influences the balance between dissolved NH_3 and NH_4^+ species in the equilibrium; pH adjustment can improve both hydrolysis and acidogenesis; biogas production is maximised. The digestion process under thermophilic conditions enhances rapid degradation of substrates. pH regulation may strengthen the buffering system to improve methane production.	Low pH may increase the volatile fatty acids (VFA) production rate which in turn inhibits the growth of methanogens and pH above 7 may induce inhibitory ammonia in the reactor. The high temperature can cause the metabolism rate of microorganisms to decline due to the denaturation of enzymes and ammonia volatilisation.	Algapani *et al.* (2019), Angelidaki and Ahring (1994), Astals *et al.* (2018) Chae *et al.* (2008), Guštin and Marinšek-Logar (2011), Latif et al. (2017), Meng *et al.* (2018), Mpofu *et al.* (2020), Valentino *et al.* (2019), Wang *et al.* (2018), Yang *et al.* (2015), Zhang *et al.* (2005), and Zhang *et al.* (2015)
Changing the C/N ratio	Improves carbon to nitrogen balance; source of nutrients to microorganisms in the reactor; the higher the C/N ratio, the higher the amount of methane produced.	The high amount of nitrogen (low C/N ratio) can lead to ammonia inhibition; high C/N ratio affects the buffer capacity by accumulating more volatile fatty acids (VFA).	Calicioglu and Demirer (2019), Choi *et al.* (2020), Mao *et al.* (2017), Puyuelo *et al.* (2011), Wang *et al.* (2012), Xu *et al.* (2018), Zeshan and Visvanathan (2012)

Method	**Advantages**	**Disadvantages**	**References**
Air stripping	The method is straightforward and usually cheap because it does not entail any of the construction facilities.	The stripping tower sometimes involves some construction costs in building the packed towers; the process is time-consuming especially when using traditional equipment; the method is inefficient to the wastewater that contains ammonia concentration above 100 mg/L.	Bonmatı and Flotats (2003), Ferraz *et al.* (2013), Huang *et al*. (2019), Karri *et al.* (2018), Li *et al.* (2020), Quan *et al*. (2009), and Yin *et al*. (2018)
Struvite precipitation	The method is convenient for the removal of ammonium (NH_4^+), phosphate (PO_4^{3-}) or both contained in wastewater.	pH, the chemical structure of the wastewater and temperature of the solution are the major factors affecting the method.	Cao *et al.* (2019), Hu *et al.* (2020), Kim *et al.* (2007), Uludag-Demirer *et al.* (2005), and Vanotti *et al.* (2020)
Membrane distillation	The large interfacial area of the membrane per unit volume offers high selectivity and efficiency of the method whereby the flow rates of gas and liquid can easily be controlled.	The method is expensive; it requires chemicals for oxidation and regeneration as part of membrane maintenance; short lifespan due to membrane fouling.	Duong *et al.* (2013), El-Bourawi *et al.* (2007), Intrchom *et al.* (2020), Qu *et al.* (2013), Tan *et al.* (2006), and Zarebska *et al.* (2014)
Ion exchange	Ion exchange materials can work under high temperature due to its high resistance to shock loadings; as a result, the time needed for regeneration can be shortened.	Frequent regeneration may incur some costs; ion exchangers are quickly saturated, leading to low performance.	Hu et al. (2020), Jorgensen and Weatherley (2003), Miladinovic and Weatherley (2008), and Tao *et al.* (2017)
Adsorption	The method demands low energy and non-frequent maintenance; it is simple and most reliable; can be operated under minimum supervision when using carbon columns. Some additives such as iron (Ferric oxide) are considered as environmentally-friendly materials which can increase methane production.	The adsorbent needs to be replaced after sometimes because the number of cycles reduces the adsorption capacity.	Al-Sheikh *et al.* (2020), Fan *et al.* (2019), Lu *et al.* (2019), Mazloomi and Jalali (2016), Novais *et al.* (2018), and Uludag-Demirer *et al.* (2005)

2.5 Methods for Removing Sulfide Inhibition during Anaerobic Digestion Process

The production of biogas during the anaerobic digestion of organic substrate may be affected by sulfide accumulation in the digester as a result of protein degradation (Yuan *et al.*, 2020). The consequences of sulfide inhibition apart from the competition between sulfur-reducing bacteria (SRB) and methane-producing archaea (MPA) during the AD process (McCartney & Oleszkiewicz, 1991), the hydrogen sulfide (H_2S) released in a gaseous form with bad odour has the tendency of corroding cooking devices when biogas used as the source of energy is contaminated with a high amount of H_2S. However, hydrogen sulfide being acidic in nature, has the tendency of interfering with the buffer system by lowering the pH of the digester, which eventually interrupts the living environment of microorganisms in the digester (Batstone *et al.*, 2015). Moreover, H_2S can certainly diffuse through cell membranes into the cytoplasm by means of cell membranes and revamp primary proteins (Dai *et al.*, 2017). In this study, several methods for alleviating the inhibition process by sulfide level accumulating in the digester have been thoroughly discussed and categorized into two processes; physicochemical and biological methods.

2.5.1 Physicochemical Procedures

The physicochemical approach in removing hydrogen sulfide in the biogas is a direct method that takes place inside the reactor by different mechanisms that involve the use of some additives such as sulfide oxidizing bacteria that are added in the reactor into which sulfide is oxidized to elemental sulfur. Other techniques involved in this approach are precipitation and scrubbing.

(i) Micro-Aerobic Process

This technique has been widely used as an effective, facile and economically viable method for hydrogen sulfide removal from biogas (Zhang *et al.*, 2019). The method involves direct aeration, i.e. applying slight quantities of air (oxygen) into an anaerobic digester (Girotto *et al.*, 2018). Studies have shown that micro-aerobic process improved the methanogenic activity as compared to the distinct and well-balanced microbial communities as noticeable from low VFAs and stable pH (Fu *et al.*, 2016).

However, there have been different terms concerning this technique. Some of the terminologies include “microaeration’’ (Duangmanee *et al.*, 2007; Jenicek *et al.*, 2014), ‘‘limited aeration’’

(Zhou *et al.,* 2007; Zitomer & Shrout, 2000), ‘‘aeration’’ (Bekmezci *et al.*, 2011; Lohwacharin & Annachhatre, 2010), ‘‘microoxygenation’’ (Díaz & Fdz-Polanco, 2012; Ramos *et al.,* 2012), ‘‘oxygenation’’ (Khanal & Huang, 2003a, 2003b) or ‘‘moderate oxygenation’’ (Van der Zee *et al.,* 2007). Generally, the terms ‘‘microaeration’’ or ‘‘microoxygenation’’ reveal the gas used. i.e. when air is injected into the anaerobic digester, the process has been referred to ‘‘microaeration’’, and when unpolluted oxygen is utilized, the term ‘‘microoxygenation’’ has been useful (Krayzelova *et al.,* 2015). The principle for hydrogen sulfide removal involves the biochemical oxidation of sulfide to elemental sulfur (S^0) or/and sulfate (SO_4^{2-}) (Krayzelova *et al.*, 2015). During this process, thiosulfate ($S_2O_3^{2-}$) may be generated in which the whole process treats sulfide as the terminal electron acceptor (Díaz *et al.,* 2011). However, when oxygen is available in a very low concentration (below 0.1 mg/L), the major end product is sulfur, as described in the equation below:

$$2HS^{-} + O2 \rightarrow 2S^{0} + 2OH^{-} \tag{5}$$

Generally, the amount of oxygen supplied in the reactor for the oxidation process of sulfide is vital in controlling the formation of sulfur and sulfate (Manconi *et al.,* 2006). For instance, it is theoretically believed that 0.5 mol O_2/mol S^{2-} is crucial for the oxidation of sulfide to elemental sulfur (Equation. 5). Meanwhile, Mora and other co-authors (Mora *et al.,* 2016), in their study, revealed that sulfide was favourably consumed and oxidized to elemental sulfur when the dissolved oxygen concentration was above 0.8 mg DO/L. This phenomenon is in agreement with the conclusion made by Ebrahim Tilahun and other colleagues (Tilahun *et al.,* 2018), the work which revealed that the formation of S^0 is highly affected by DO concentrations. However, besides the amount of oxygen required to enhance the micro aeration process, there are other important factors that should be considered for an effective micro-aeration method, such as oxygen transfer rate (OTR) and oxygen utilization rate (OUR) (Nguyen & Khanal, 2018). The two processes are regarded as limiting factors since they play a key role in providing an adequate amount of oxygen required for sulfide removal in the reactor. The factors determining the OTR during the AD process include reactor configuration, micro-aeration technique (i.e., use of air or oxygen, bubble size, injection in aqueous or gaseous phase), total solids (TS) gratified of the substrate in the reactor, etc. (Garcia-Ochoa & Gomez, 2009). For instance, it was observed that the micro-aeration process was unsuccessful during the removal of sulfide in the liquid phase when the diffusion of air/oxygen was limited in the reactor (Sheets *et al.,* 2015). On the other hand, the OUR in micro-aeration during the AD process is influenced by the inoculum used and substrate fed to the reactor. For example, it was discovered that a specific oxygen dosing control is required for the microaeration process involving substrates with a high rate of hydrolysis, such as lignocellulosic biomass (Nguyen & Khanal, 2018). In practice, when the oxygen amount is controlled, it enhances the prevention of excess accumulation of VFA in the reactor, which in turn increases the methane yield (Jun & Jing, 2013; Xu *et al.*, 2014). However, the method still needs critical and thoroughly analysis primarily on the determination of micro-aeration rate to be employed on a specific reactor for complete oxidation of soluble substrates.

(ii) Precipitation Process

The precipitation method has been among the prominent approaches to treat wastewater containing sulfur by using metals with high affinity to sulfur, such as iron and zinc. This method involves the summation of metal salts with iron, zinc, lead and copper salts to precipitate sulfide, which forms a highly insoluble metallic sulfide precipitates (Padival *et al.*, 1995; Poulton *et al.,* 2002). Treating metal-containing wastewaters with sulphate reducing bacteria (SRB) has promise as an alternative over chemical methods. The Fe^{3+} is forceful in reducing sulfide in the liquid phase. Fe^{3+} oxidizes sulfide to elemental sulfur, although being reduced into Fe^{2+}, which precipitates with sulfide to form ferrous sulfide precipitants (Dohnalek & FitzPatrick, 1983).

$$2Fe^{2+} + S^{2-} \rightarrow 2Fe^{2+} + S^{0} \qquad (6)$$

$$Fe^{2+} + HS^{-} \rightarrow FeS \ + H^{+} \qquad (7)$$

For instance, the study which was done by Lishan Zhang and other co-authors (Zhang *et al.*, 2009) revealed that Ferric iron is typically used for sulfide precipitation in sewers, hence attaining corrosion and odour control. Through this study, it was discovered that the process of controlling sulfide has an influence on the actions of sulfate-reducing bacteria and methanogens in anaerobic sewer biofilms. The dosage of Fe^{3+} during precipitation of sulfur in the liquid phase was found to considerably prevent sulfate reduction and methane production by sewer biofilms. The effluent discharged from the reactor was found to have a higher concentration of sulfate as an end product due to the precipitation reaction induced by Fe^{3+} dosage. The reduction of sulfide concentration in the reactor was nearly 60%, the results which show that constant addition of Fe^{3+} would minimize the need for ferric salts as a potential solution to reduce sulfide inhibition. Additionally, in some cases, it has been discovered that the precipitation reaction is not much influenced by ferric iron. For instance, this 60% sulfide removal can be achieved at a shorter time scale of 1.5s provided that the pH for wastewater is around 7, and a stoichiometric ratio around 14 mol Fe(II) (mol S(-II))$^{-1}$ (Kiilerich *et al.*, 2017). The investigation on the consequence of pH during precipitation reaction shows that when the pH is below 7, typically less than 40% of the added ferrous iron can induce sulfide precipitation. However, when the pH is above 8, the result shows that exhaustive precipitation of all the supplementary ferrous iron can be achieved (Nielsen *et al.,* 2008). It is therefore, recommended that the ferric-iron-to-ferrous-iron ratio should be a 1:1 mixture of ferric chloride and ferrous sulfate for an improved precipitation reaction efficiency. Nonetheless, higher sulfide removal efficiencies of 96–99% were obtained under physicochemical method using ordinary coagulants which were incomplete precipitant [$FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$] and coagulant-aids [$Ca(OH)_2$ and $CaCO_3$] were used to both raw and sulfide added wastewater (Altaş & Büyükgüngör, 2008).

(iii) Adsorption of H_2S on Activated Carbon

Adsorption is a simple procedure that exploits physical and chemical processes for the emptying of natural air and water, thus removing the adsorbed material in the form of adsorbate (Abdel *et al.*, 2015; Sadegh *et al.,* 2017). Lately, adsorption on AC originated from organic gears can be considered as an impressive technique to eliminate contaminants from wastewater due to its affordability. The AC has been applied for eradicating H_2S from gas mixture and liquid. Normally, the adsorption process and its capacity depend on various aspects such as porosity, surface area, functional groups, activation method, and adsorbate conditions. To improve the adsorption capacity, it is decisive to examine the structure of raw materials and the appropriate activation agent that can augment the chemistry of the adsorbent surface. The diversity of impregnated agents have been in use to reinforce the adsorption capacity of AC in H_2S removal, e.g. impregnated with iodine (Marsh & Reinoso, 2006), metal hydroxides and oxides (Bashkova *et al.,* 2009; Cui *et al.,* 2009; Li *et al.,* 2008), carbonates (Chen *et al.,* 2010) and nitrogen groups using urea or melamine (Seredych & Bandosz, 2008). Several studies have shown that chemically AC is more effective with high performance in adsorption. For example, the results showed that the chemical activation of palm shell AC by H_2SO_4 or KOH activation performed better than the thermal activation by CO_2 (Habeeb *et al.*, 2018). However, in most cases the technology of AC has been limited to saturation of the pores, which demands regular replacement and regeneration. Different methods and techniques have been applied in order to enhance the performance of AC during the adsorption process. For instance, controlled steam pretreatment is used to develop the surface of activated carbon (AC), in which the steam-treated AC electrode displays superior electrochemical properties. The findings from work done by Zhen-YuLi and other colleagues revealed that the steam pretreatment at 700 °C followed by hydrogen (H_2) gasification was found to be a sufficient condition for augmenting the surface area pore size and pore volume of AC (Li *et al.*, 2017). The reported steam-treated AC electrode shown the tremendous stability of 92% initial capacity after 1000 cycles. Other techniques based on chemical methods for surface improvement of the AC are costly due to the demand for alterations and the number of acidic and basic surface groups on the surface of activated carbon. However, it has been found that the surface chemistry of AC can be enhanced through the impregnation of the AC with other functional materials such as metal oxide and the addition of transition metal elements to make composite materials (Habeeb *et al.*, 2018). For example, Seredych and other co-authors, in their study, discovered that the surface chemistry of the carbonaceous adsorbents could also be enriched by adding some transition metals for sulfide removal. This study affirmed a series of hydroxide composites or metal oxide with graphite oxide (GO) that can influence the adsorption process of H_2S. Meanwhile, Nguyen-Thanh and Bandosz, in their study, examined the effects of bentonite clay binders encompassing copper, zinc, or iron in the interlayer spaces on the efficiency of the adsorbents in H_2S removal. It was then reported that the adsorbent capacity of AC could be enhanced by surface reformation with a copper-containing binder, thereby signifying how the oxygenated surface groups were augmenting the adsorption process (Nguyen-Thanh & Bandosz, 2005).

The importance of composite materials mixed in different amounts was shown by Adil Ansari and other co-authors in their study in which they evaluated the influence of the synergetic effect of surface chemistry and porosity of sewage sludge obtained from materials endowed with carbonaceous phase on their effectiveness in removing hydrogen sulfide. The results indicated that mixing the polymer with sludge increases the amount of H_2S adsorbed/oxidized when compared with the adsorbents obtained from pure precursors (sludge or polymer). The higher performance of the material is induced by the catalytic centres for hydrogen sulfide oxidation derived from sewage sludge, whereas a carbonaceous phase plays a foremost part in increasing the dispersion of catalytic centers by providing additional ‘‘storage space’’ in its micropores (Ansari *et al.,* 2005).

(iv) Stripping Method

Stripping is another method involved in sulfide removal, treated as a physical system in which air and wastewater are passed as counter currents. The system is advantageous since it is economical and produces energy in the form of biogas with less sludge production (Kinidi *et al.,* 2018). This method encompasses the development of a stripper, which is proficient in removing sulfide from wastewater undergoing anaerobic digestion without varying the chemical characteristics of the wastewater. For example, it was reported that the sulfide removal efficiency of 60 – 70 % was achieved through an innovative stripper which was designed in the laboratory with optimized parameters involved during the design and operation, such as airflow rate, liquid flow rate, liquid to air ratio, and pH profile (Rao *et al.,* 2003). In this experiment, it is very crucial to optimize the inlet air required per amount of sulfide during the designing process of the stripper. The air stained with traces of hydrogen sulfide has to be refined using a proper system such as a biofilter before being released to the atmosphere (Furusawa *et al.,* 1984). The process is initially based on air recycling in which the recycled air emitted in the atmosphere contains a traces amount of hydrogen sulfide. The recycling process of wastewater from the stripper, which may include a reduced concentration of free H_2S, can be regarded as a controlling method of sulfide concentration in the anaerobic reactor.

On the other hand, results from the study which was done by Glória and other co-authors (Glória *et al.,* 2016), air stripping technique showed that hydrogen sulfide removal efficiency was in the range of 40 – 60%. The results further indicated that the rate of air injected into the reactor did not affect the dissolved methane removal efficiency.

However, this method is not economically feasible as it requires the construction of the costly stripping tower.

(v) Wet Scrubbing

Wet scrubbing, sometimes known as chemical scrubbing or absorption, encompasses contaminant mass transfer in the liquid phase and successive reactions with acidic, basic, or oxidant reagent(s). In most cases, sodium hypochlorite (NaClO) is used to oxidize H_2S in alkaline media (pH >9):

$$H_2S + 4NaOCl + 2NaOH \rightarrow Na_2SO_4 + 4NaCl + 2H_2O \qquad (8)$$

(Biard *et al.,* 2010).

From the study done by Biard et al. (2010), on the performance of the scrubber with a contactor made of a wire mesh packing structure with liquid and gas flowing co-currently at high velocity (>12 ms^{-1}), it was informed that hydrogen sulphide removal efficiency of 95% could be attained. This high removal efficiency is accompanied by residence time in the scrubber being dropped to 30 ms using a NaOCl caustic scrubbing solution. From the results, it can be concluded that both hydrodynamic and chemical conditions automatically induce H_2S removal. However, Yan Wang and other colleagues (Wang *et al.*, 2020), in their study, employed hydrogen peroxide (H_2O_2) as one of the oxidizing agent and urea as an alkaline media to investigate its performance on H_2S removal efficiency. In this study, high purity gases of H_2S and N_2 were used to prepare a simulated gas. The H_2S inlet concentration was adjusted based on the modification of H_2S and N_2 flowmeters. The H_2S analyzer (less than 2% repeatability error and measurement limit is 0.1 ppm) was used for the analysis of H_2S concentration before and after the separate test. De-ionized water and 30% H_2O_2 solution were treated to formulate a 500 ml H_2O_2/urea blended solution. The HCl and/or NaOH solutions were added to the mixture of H_2O_2/urea to regulate the pH of the solution. The temperature fluctuations were controlled by using a thermostatic water bath and thermometer. Meanwhile, the pH value of H_2O_2/urea solution was controlled by applying the Peristaltic pump and solution tanks containing-HCl and/or NaOH. The simulated gas with H_2S entered the Vacuum Ultraviolet (VUV)-spraying scrubber when the temperature and the pH value of H_2O_2/urea mixed solution were effectively fixed to the required data. The VUV-spraying scrubber was then used to facilitate the photochemical oxidation reaction following the activation of the VUV lamp. The VUV-spraying scrubber, defined as the outlet concentration of H_2S was used to analyze the concentration of H_2S. Every experiment was controlled at 20 min in which the amount of H_2S recovered was recorded once per minute. However, when a process parameter or factor was studied, an optimized single factor research method for process parameter was adopted, while other parameters or factors remained constant (Wang *et al.*, 2020). Results showed that the maximum H_2S removal efficiency was 98.2% under optimal experimental conditions. It was revealed that H_2S removal efficiency increased as the UV-light intensity and solution pH were improved. In this experiment, the change of the H_2O_2 concentration from 0 to 0.2 mol/L influenced the increase in H_2S removal efficiency firstly at (38.7% – 98.2%) and then reduced to (98.2% – 90.1%). These results are in agreement with several studies which stated that the SO_2 removal efficiency was almost 100% in the wet-scrubbing process because of the high solubility in water (Hao *et al.*, 2016; Sun *et al.*, 2011; Yoon *et al.*, 2016; Zhao *et al.*, 2015). Additionally, this method, despite being widely used due to its simplicity in operation and high efficiency. However, the use of different absorbers requires high regeneration energy input and strong equipment corrosiveness (Chen, 2017; Wang*et al.,* 2020). Nevertheless, chemical scrubbing in packed towers may incur some operating costs, which involves the construction of high and large wet scrubbers (Couvert *et al.,* 2008).

2.5.2 Biological Methods

Numerous physicochemical procedures have been in use to eradicate H_2S from industrial waste gas streams such as absorption (Boumnijel *et al.*, 2016; Taheri *et al.*, 2016), scrubbing (Liu & Wang, 2019), and using chemicals that are water-containing (Kang *et al.,* 2020; Li *et al.,* 2019). Nonetheless, these operational procedures are costly and induce the production of chemical wastes. Alternatively, different biological treatment processes such as autotrophic denitrification (Vaiopoulou *et al.*, 2005) and biological desulfurization (Cano *et al.,* 2018) have been adopted over other methods due to the mild running conditions of the method and its affordability.

Through different electron acceptors, the biological sulfide removal method in wastewater can be split into aerobic biological technology and anaerobic (or anoxic) biological technology. In aerobic technique, oxygen is usually used as electron acceptor whereas, on anoxic technique, nitrate or nitrites are used as electron acceptors (Cai *et al.,* 2017).

(i) Aerobic Biological Technology

In this method, several studies were done in which the amount of dissolved oxygen in the digester containing wastewater for sulfide removal was studied. For instance, Guerrero et al. (2016) in their study, they realized that the removal efficiency of sulfide under aerobic condition is influenced by the ratio of oxygen and sulfide, governed by the following chemical reactions:

$$H_2S + \frac{1}{2}O_2 \rightarrow S^0 + H_2O \qquad (9)$$

$$S_0 + H_2O + \frac{3}{2}O_2 \rightarrow SO_4^{2-} + 2H^+ \qquad (10)$$

$$H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^{+} \tag{11}$$

This approach showed that a maximum of 90% sulfide removal could be achieved at optimal dissolved oxygen. From the results, it is evident that partial oxygen can induce maximum sulfide removal efficiency. However, these results are complying with the findings of other researchers, such as Doğan and other co-authors (Doğan *et al.,* 2012). They run biological sulfide oxidation by operating an airlift reactor when oxygen-limiting conditions were in the range of 0.2 – 1.0 mg/L. In this study, it was found that as the volumetric sulfide loading rate was increased, elemental sulfur production was also elevated with over 93% sulfide removal.

Nonetheless, the whole process of bubbling aeration is ascertained as a very difficult procedure which sometimes leads to stripping of hydrogen sulfide in the water, which results into bad odour and making the sulfide recovery process difficult (Kampschreur *et al.,* 2009; Sun *et al.,* 2017). Apparently, there have been other factors that affect the rate of sulfide removal efficiency in the reactor containing wastewater. Several studies have reported the influence of pressure during mass transfer (Liu *et al.,* 2015) and the accumulation of volatile fatty acids in the reactor, which lowers the amount of sulfur oxidation to sulfate resulting in the increased sulfur production (Celis-García *et al.,* 2007). It was then discovered that silicone membranes could control the mass transfer by regulating the amount of pressure and airflow. This process enhanced sulfide removal efficiencies to about 96% in a combined anaerobic/microaerobic reactor where substantial sulfate production did not occur (Cai *et al.,* 2017).

On the other hand, the increase of biogas to air ratio and retention time were other essential factors evaluated and suggested to influence the sulfide removal efficiency. From the study done by Chaiprapat and other co-authors, it was reported that the biogas to air ratio of 1:4 was suitable for H_2S removal in which the average reductions for the biofiltration system reactor were 94.7%, 87.3%, 85.6% at a retention time of 160, 80 and 40 s, respectively (Chaiprapat *et al.,* 2011).

(ii) Anaerobic (anoxic) Biological Technology

Anoxic mechanism refers to a process in which the denitrifying microorganisms consume nitrate as a means of sulfide removal by oxidation of sulfide. Since wastewater contains an insignificant amount of nitrite and nitrate, these concentrations are initially injected into the digester artificially in the course of the sulfide removal process (Soreanu *et al.,* 2008). The introduction of nitrate in the digester allows the potential reduction of sulfide since the nitrate-reducing bacteria overwhelms the sulfate-reducing bacteria during competition between the two microbes (Kotu *et al.,* 2019). In most cases, autotrophic denitrification has been widely adopted during desulfurization process in which sulfide oxidizing bacteria (SOB) uses sulfide as an electron donor to couple with nitrate reduction (Cui *et al.,* 2019). As a result, elemental sulfur is obtained as an intermediate product when sulfide is oxidized to sulfate. The reactions governing anoxic method are summarized below (Li *et al.,* 2009):

$$5S^{2-} + 2NO_3^- + 12H^+ \rightarrow 5S + N_2 + 6H_2O \quad \Delta G^{\theta} = -955\ \text{kJ/reaction} \tag{12}$$

$$5S + 6NO_3^- + 2H_2O \rightarrow 5SO_4^{2-} + 3N_2 + 4H^+ \quad \Delta G^{\theta} = -2738\ \text{kJ/reaction} \tag{13}$$

$$3S^{2-} + 2NO_2^- + 8H^+ \rightarrow 3S + N_2 + 4H_2O \quad \Delta G^{\theta} = -917\ \text{kJ/reaction} \tag{14}$$

$$3S + 6NO_2^- \rightarrow 3SO_4^{2-} + 3N_2 \quad \Delta G^{\theta} = -2027\ \text{kJ/reaction} \tag{15}$$

Among the studies done to explore the efficiency of anoxic technique in removing sulfide concentration in wastewater was that one presented by Yang and other co-authors (Yang *et al.,* 2005) in which batch tests were considered and operated to study both chemical and biological sulfide oxidation by nitrate in the liquid phase. Results indicated that sulfide oxidation was biologically controlled through anoxic conditions in which elemental sulfur was recovered as the end product during the process. However, nitrite was accumulated in wastewater as an intermediate product. Moreover, Zeng *et al.* (2018) from their study, reported that the loading rate could influence the sulfide removal efficiency. In their findings, the removal efficiencies of both H_2S and $NO_x^- - N$ were 84% and 61.9%, respectively, at an average loading rate of 30.67 g-H_2S $m^{-3}h^{-1}$. However, results indicate that the removal efficiencies were dramatically dropped as the loading rate was decreased. For instance, the efficiencies of 61.9% (average removal capability of 22.42 g-H_2S $m^{-3}h^{-1}$) and 49.2% were recorded respectively when biogas slurry was used. This elimination capacity is in agreement with the results from the study which was done by Mouna and fellow co-authors to evaluate the effect of numerous parameters, such as H_2S concentrations, Empty Bed Residence Time (EBRT) and molar ratio N/S, on the performances of biofilters under anoxic conditions. In this study, it was found that at an EBRT of 300 s, elevated schist proficiently treated H_2S concentrations up to 1100 ppmv (maximum removal capability RCmax = 30.3 g-H_2S m^{-3} h^{-1}) (Jaber *et al.*, 2017).

Meanwhile, in the work which was done by Qaisar Mahmood and other co-authors (Mahmood *et al.*, 2007), in testing the ability of anoxic sulfide oxidizing (ASO) reactor for instantaneous sulfide and nitrite removal from wastewaters, it was reported that the removal efficiencies of nitrite and H_2S in the anoxic sulfide reactor made of perspex with a working volume of 1.3 L were found to be 75% and 99% respectively. The results reported were for 15 days of operation in which the sulfide loading rate was an essential index to evaluate the proficiency of a bioreactor. Generally, it was discovered that both loading rate, substrate concentration and hydraulic retention time (HRT) plays a major role in determining the potential of the reactor and removal efficiencies of both nitrite and H_2S. In practice, when the sulfide loading rate was in the range of 0.02 – 0.96 kg/(m^3 day), the sulfide removal percentage was above 88.97%. However, during the final 15 days of operation, there was a moderate reduction in sulfide removal percentage due to an increase of expulsion sulfide concentrations which raised to 211 mg/L. On the other hand, the effect of hydraulic retention time showed that the maximum removal rates of both sulfide and nitrite were reached at 13.82 and 16.311 (kg/m^3 per day), respectively, at 0.10 day HRT. Conclusively, the reactor performance was improved when HRT was decreased at a fixed substrate concentration than when the substrate concentration was increased at a fixed HRT.

Furthermore, the molar ratio of sulfide/nitrate (S/N) is another important determining factor on biogas desulfurization performance in anoxic bioreactors. Several studies have indicated that H_2S is oxidized into elemental sulfur when the amount of NO_3^- is not sufficient. However, when the amount NO_3^- is adequate, a complete oxidation process of H_2S to sulfate occurs (Jing *et al.*, 2009; Manconi *et al.*, 2006). This phenomenon displays how the S/N molar ratio is very crucial during H_2S oxidation. From the work which was done by Li *et al.* (2016), to examine the effect of the molar ratio of sulfide/nitrate (S/N) on biogas desulfurization process in a biotrickling filter (BTF) and a biobubble column (BBC), it was revealed that the removal efficiencies of H_2S improved from 66 to 100 % upon decreasing the S/N ratios from 3.6 to 0.7. Meanwhile, the BTF showed the most stabilized desulfurization process than the BBC, a phenomenon which could have been attributed to the difference in gas-liquid contacting modes of both BTF and BBC. In this study, it was then concluded that different methods for injecting nitrate in wastewater, i.e., both infrequent and frequent, did not affect the exclusion of H_2S

considerably. In contrast, the infrequent inclusion of nitrate wastewater elevated the percentages of sulfate recovery and the performance denitrification process.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Sample Collection, Pretreatment and Preparation

Materials used in this study includes the pH meter, Hach DR 2800 portable spectrophotometer, BOD incubator, COD reactor, GEOTEC Biogas 5000 analyzer, Thermo Scientific 1200 Box Furnace, Batch-reactor of 10 liters capacity and sieve no.16 of 250µm.

The substrate used in this experiment was a liquid mixture of blood and intestine discharged from slaughterhouse waste point owned by Arusha Meat Company Limited, located in Arusha City, Tanzania. The sample was then stored in a freezer at 4 °C before characterization. The substrate stored was inoculated with 10% (w/v) of cow dung, which was obtained from cattle keepers. During phase I of AD, the mixture was fed into 10 litres batch-reactor capacity constructed using stainless steel materials for biogas production and performance evaluation of the reactor for the duration of 68 days. This batch-reactor (Figure 3.1) was operated at 37 °C temperature, monitored daily for quantification of biogas produced and measurement of different parameters such as pH, sulfide concentration, ammonia nitrogen and VFA and alkalinity. These parameters were analyzed from 200 mL of a sample taken from the reactor after every seven days.

However, during phase II of AD process, the mixture was then fed into one litre batch-reactor capacity for biogas production. Adsorbent materials used in this study were soil samples obtained from two different locations. The red rock sample was collected from Nayobi village, Ngorongoro district, Arusha, Northern Tanzania (2°43′17.9″S 35°27′35.2″E) whereas the anthill soil sample was collected from anthill around the campus of Nelson Mandela African institution of Science and Technology (NM-AIST), Arusha, Tanzania (3°23′56.4″S 36°47′49.8″E). The two types of soil samples were processed into powder form prior to further analysis. The red rock was pulverized to 250 µm fine particles and calcinated in the furnace (Thermo Scientific 1200 Box Furnace) at 700 and 900 °C for 2 hours with a ramp rate of 10 °C/min. The calcined samples were allowed to cool to room temperature and processed further by grinding and sieving using sieve no.16 of 250 µm before further analysis. Similar procedures were followed to process the anthill soil sample. The obtained calcined adsorbent materials were kept in a clean container and labelled as AHX and RRX, where the prefixes

“AH” and “RR” denotes anthill and red rock respectively. The postscript “X” represents the calcination temperature.

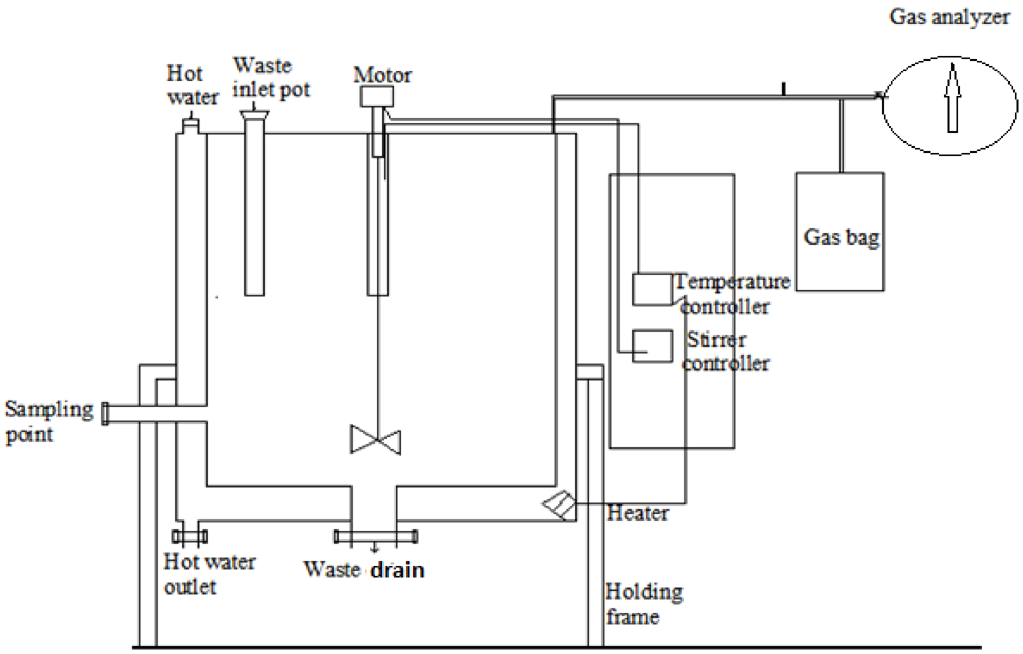

Figure 1: Batch – reactor for Phase I anaerobic digestion

3.2 Analytical Methods

Both total solids (TS) and volatile solids (VS) were determined by using standard protocols for wastewater examination (APHA, 2015). The HACH DR2800 instrument (HACH, Loveland, CO) was used to measure chemical oxygen demand (COD) using HACH digestion solution vials for high range COD (20 mg/L to 1500 mg/L) following the manufacturer’s protocol (Grimberg *et al.*, 2015). On the other hand, biological oxygen demand (BOD_5) was also measured using the OxiTop method in which the stored values were quantified in mg/L after 5 days. All measurements for both COD and BOD were performed in triplicate. Ripley and Kapp titration methods were used to determine the concentrations of volatile fatty acids (VFA) and alkalinity (Mota *et al.*, 2015). The pH of the samples was measured using a VWR symphony pH meter. The concentrations of total ammonia nitrogen (TAN) and sulfide in the liquid phase were ascertained by the Nessler method and methylene blue method, respectively (Harwood & Kühn, 1970; Strocchi *et al.*, 1992). Liquid samples were collected and then centrifuged at 8000 rpm for 15 min and then filtered through 0.45 µm Whatman filter paper. The filtrate collected was then used to measure the parameters such as pH, VFA, total ammonia and alkalinity. Methane content was determined using biogas analyzer i.e. Geotec Biogas 5000. The summation of both unionized [NH_3–N] and ionized [NH_4^+] forms of ammonia was used to quantify the total ammonia nitrogen (TAN) by the Equation (16) below (Richard *et al.*, 2019):

$$[\mathrm{TAN}] = [\mathrm{NH_3} + [\mathrm{NH_4}^+] \tag{16}$$

The adsorption capacity was calculated using a mass balance according to the Equation:

$$\mathrm{Q_e} = \frac{(\mathrm{C_o} - \mathrm{C_e})\mathrm{V}}{\mathrm{m}} \tag{17}$$

Where Q_e is the mass of TAN/S^{2-} exchanged per unit mass of adsorbent mixed at different ratios (mg/g), C_0 and C_e are initial and equilibrium concentration of TAN/S^{2-} in the liquid phase (mg/L), respectively, V is the volume of the slurry mixture (L) and m is the mass of adsorbent (g).

The adsorbates' (TAN and S^{2-}) removal efficiency were computed using the Equation:

$$\text{Removal efficiency (\%)} = \frac{(\mathrm{C_o} - \mathrm{C_e})100}{\mathrm{C_o}} \tag{18}$$

Where; C_0 (mg/L) is the initial concentration of TAN/S^{2-} in the liquid phase, C_e (mg/L) represents equilibrium concentration of TAN/S^{2-} in the liquid phase. All these laboratory analyses were carried out at the Nelson Mandela African Institution of Science and Technology (NM-AIST), Arusha, Tanzania.

Figure 2: Slaughterhouse waste discharging point

Figure 3: Geotech Biogas 5000 analyzer

3.2.1 Adsorbent Characterization

The mineral phases present in the adsorbent materials were elucidated by employing powder-X-ray diffraction (p-XRD). The analyses were performed in the high angle 2θ ranging from 5 to 55° using a Bruker AXS D8 Advance X-ray diffractometer equipped with a nickel-filtered Cu Kα radiation (λ=1.7890Å) at 40 kV, 40 mA and at room temperature. The scan speed was 0.5 sec/step at an increment of 0.01314. Nitrogen adsorption-desorption isotherms were assessed at 77 K by using a porosimeter (Nova 4200e Quantachrome, UK) after degassing the sample at 160 °C for 3 hrs. About 0.1 g of the calcined soil sample was used for an adsorption-desorption process at a temperature of -195.8 °C. The textural properties of both red rock and anthill soil samples were analyzed by using Brunauer-Emmett-Teller (BET) method to determine the specific surface area while pore size and pore volume were valuated through Barrett-Joyner-Halenda (BJH) method. The infrared spectroscopy measurements (FT-IR, Perkin–Elmer, Spectrum 100) were done to identify the vibration frequency in the functional groups of the adsorbent materials. The wavelength of the spectra was obtained in the range of 400 and 4000 cm^{-1}. Sample's chemical composition was performed at the Geological Survey of Tanzania (GST) by employing X-ray fluorescence analyzer (XRF), model Vanta Element Series manufactured by Olympus Scientific Solutions, USA. The surface microstructure and morphology of the calcined samples (AHX) and (RRX) were investigated using Zeiss Ultra Plus Field Emission Scanning Electron Microscopy (FE-SEM) from The University of Cape Town, South Africa.

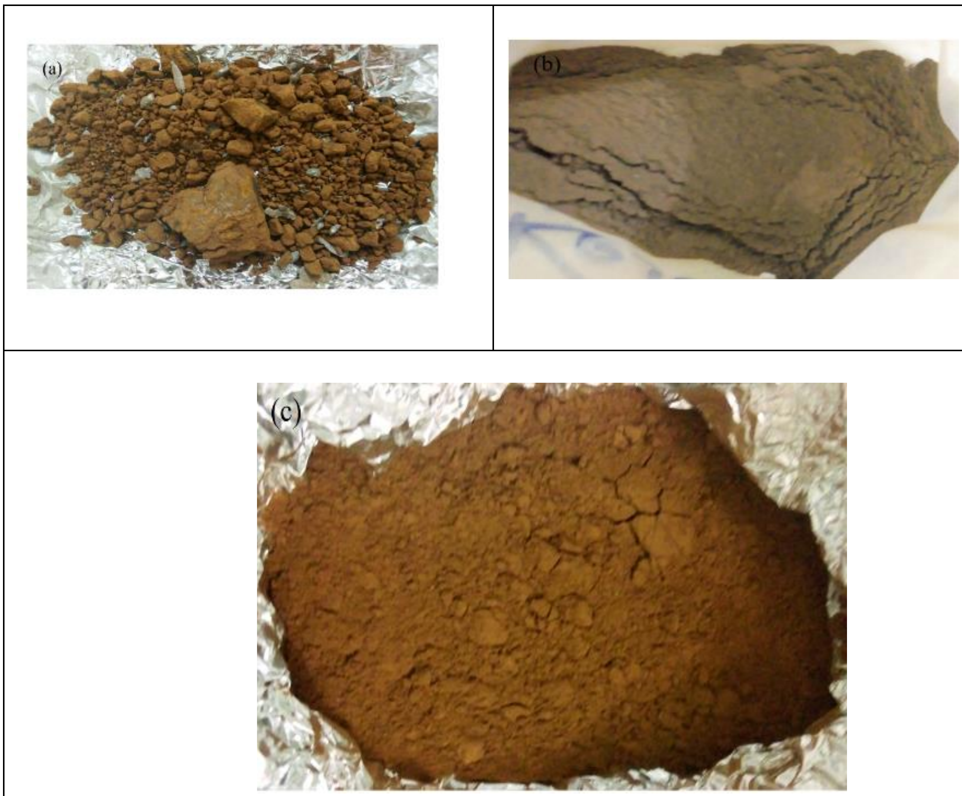

Figure 4: Adsorbent samples from (a) red rock soil (b) Fine powder of anthill soil (c) Fine powder of red rock soil

3.2.2 Experimental Setup for Phase II Anaerobic Digestion

During phase II of anaerobic digestion, side-arm conical flasks (Pyrex) of 1L capacity fed with slurry (a mixture of abattoir waste and 10% w/v cow dung inoculum) to about 900 mL were used as batch reactors. The remaining 100 mL was used as headspace volume. The reactors were immersed into three thermostat water baths operated at 37 ℃ and labelled as A, B and C.

Each of the three thermostat water baths were equipped with three reactors. Reactors in water bath A were used as control of the experiment which were run in triplicate. The reactors in the respective water baths were named as A1, A2, A3; B1, B2, B3; and C1, C2, C3. Each reactor was connected to a 1L Tedlar gas sampling bag. Then, the experiment was run, and the anaerobic digestion was allowed to proceed for 65 days to monitor the level of dissolved ammonia and sulfide inhibition as well as methane production before and after the addition of inorganic additives for adsorption process. Shaking of reactors was done twice a day at 10:00 AM and 10:00 PM. After 44 days of the initial AD process, adsorbent materials (AHX and RRX) for adsorption of TAN and sulfide concentrations were applied in each reactor at the mixed ratios of 1:1, 1:2 and 3:1 (AH:RR). This was followed by another 20 days of monitoring the removal efficiency and the impact of each reactor composition on methane production. Reactors in water bath A which were used as a control experiment, those in water bath B and C were supplied with adsorbent materials calcined at 700 and 900 °C, respectively. The adsorbent material (4 g) was contacted with 1 L of the substrate containing the adsorbate under study. The resulting mixture was shaken well for 5 minutes followed by varying the contact time at intervals of 5, 10, 15, 20, 30, 60, 90, and 120 min. Measurements of all parameters and methane content were done after every 7 days.

3.2.3 Adsorption Isotherm Studies

The adsorption capacity for the uptake of TAN and sulfide by AH @RR adsorbent were studied by Langmuir (4), Freundlich (6) and Jovanovich (7) isotherm models in accordance with experimental data. The equilibrium behaviour of TAN and sulfide exchange with the adsorbents in different ratios were characterized by fitting the model equations to the experimental data. The Langmuir adsorption assumes that the adsorbent’s surface is uniform (monolayer) with no interaction between adsorbed and desorbed molecules which exist in equilibrium. On the other hand, Freundlich isotherm describes the existence of multisite adsorption on rough (heterogeneous) surfaces. In Jovanovich model, the assumptions considered are the same as in the Langmuir model. However, the possibility of mechanical contact between adsorbent and adsorbates is mostly taken into consideration in this model (Al-Ghouti & Da'ana, 2020; Al Jaberi *et al.*, 2020).

The linear Langmuir Equation is written as:

$$\frac{C_{eq}}{q_e} = (\frac{1}{q_{max}})C_{eq} + \frac{1}{k_L q_{max}} \tag{19}$$

Where q_e (mg/g) is the amount TAN/S^{2-} adsorbed at equilibrium, q_{max} (mg/g) is the maximum adsorption capacity, C_{eq} (mg/L) is the concentration at equilibrium, C_o is the initial concentration, and k_L (L/mg) is the Langmuir Equilibrium constant.

$$R_L = \frac{1}{1 + K_L C_o} \tag{20}$$

The linear Freundlich Equation is written in the following form:

$$q_e = k_f . C_{eq}^{1/n} \tag{21}$$

Where q_e (mg/g) is the amount TAN/S^{2-} adsorbed at equilibrium, C_{eq} (mg/L) is the concentration at equilibrium, k_f (mg/g) is the Freundlich capacity coefficient, and 1/n is the measure of adsorption intensity. However, Equation (6) above is further deduced to equation (7) below for quantification of parameters.

$$\log q_e = \frac{1}{n} \log C_{eq} + \log k_f \tag{22}$$

The linear Jovanovich Equation is written in the following form:

$$\ln q_e = \ln q_{max} - K_J C_{eq} \tag{23}$$

Where q_e (mg/g) is the amount TAN/S^{2-} adsorbed at equilibrium, q_{max} (mg/g) is the maximum adsorption capacity, C_{eq} (mg/L) is the concentration at equilibrium, K_J (l/g) is the Jovanovich constant.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Substrate Characterization

The substrate mixture was characterized before introduced into the reactor for analyzing parameters such as TS, VS, COD and BOD. The amount of TS, VS, COD and BOD in the raw substrate for phase II of AD process was found to be 0.93%, 78.09%, 11025 and 1600, respectively. Characterization was also done after 65 days of digestion process where the amount of TS, VS, COD and BOD was found to be 3.59%, 68.12%, 1575 and 375 respectively. The VS removal efficiency during day 65 was 12.77%. The increase in TS was due to the addition of inorganic additives in the reactor during day 44 of AD.

Table 5: Table Characteristics of slaughterhouse waste mixed with cow dung before and during 68 days of phase I of anaerobic digestion

	TS (mg/L)	VS (mg/L)	COD (mg/L)	BOD_5 (mg/L)	VFA (mg/L)	Alkalinity (mg/L)	Ratio (VFA/Alk)	pH	Temperature (°C)
Day 1(in)	5241	3983	11025	1600	149.15	207.15	0.72	7.7	37
Day 13					205.2	380	0.54	7.69	37
Day 22					243.53	529.41	0.46	7.65	37
Day 30					361.23	903.08	0.4	7.5	37
Day 37					300.18	811.29	0.37	7.51	37
Day 44					258.58	861.93	0.3	7.6	37
Day 52					198.65	735.74	0.27	7.61	37
Day 60					162.72	813.6	0.2	7.68	37
Day 68	2322	912	1575	375	150.92	943.25	0.16	7.72	37

Table 6: The percentage composition of gas

DAY	%CH_4	%CO_2	%O_2	Balance	H_2S (ppm)
Day 1	0	0	0	0	0
Day 5	1.1	4.2	13.8	80.9	12
Day 13	46.8	24	3.6	25.6	2
Day 22	57.6	31.7	2.7	7.9	4
Day 30	62.5	27.8	3.1	6.6	17
Day 37	69.6	26.2	2.6	1.6	119
Day 44	65	31.6	2.4	1.0	108
Day 52	42.6	33.8	2.2	21.4	112
Day 60	37.3	27.9	2.4	32.4	124
Day 68	24.6	20.7	2.5	52.2	132

4.2 Digester's Performance

The performance of the digester during phase I was evaluated by considering the characteristics of the waste which was undergoing anaerobic digestion for the duration of 68 days in relation to the biogas produced. The accumulation of volatile fatty acids (VFA) and alkalinity as indicated in Table 5, there was a variation from day 1 to day 30 (29 days) in which there was an increase in VFA level from 149.15 mg/L to 361.23 mg/L equivalent to 57.53% increase. In contrast, there was a slight decrease in pH from 7.7 to 7.51. The reduction in pH didn't reach below 7 which is the minimum requirement for digester's stability and methanogenic activity, and the alkalinity was maintained at the level which didn't affect the whole digestion process (Li *et al.*, 2014). The high level of VFA increase in the first 29 days (51.4%), shows that it was during the process of acidogenesis in which the organic matter was being degraded to acids and alcohols which are regarded as a source of food for microorganisms.

Table 7: The accumulation of different forms of ammonia and sulfide in relation to methane content

DAY	NH_3–N(mg/L)	NH_4^+(mg/L)	TAN (mg/L)	S^{2-}(mg/L)	pH (digester)	%CH_4
Day 5	428.22	614.87	1043.09	32.6	7.7	1.1
Day 13	420.5	608	1028.82	27	7.69	46.8
Day 22	418.75	612.5	1031.25	12.78	7.65	57.6
Day 30	400.8	622.82	1023.62	9.02	7.5	62.5
Day 37	415.2	620.62	1035.82	14.66	7.51	69.6
Day 44	519.19	590.89	1110.08	11.04	7.6	65
Day 52	512.8	582.82	1095.62	12.67	7.61	42.6
Day 60	539.5	570.22	1109.72	14.82	7.68	37.3
Day 68	615.82	492.12	1107.94	11.43	7.72	24.6

Meanwhile, in the last 30 days, the VFA level decreased from 300.18 mg/L to 150.92 mg/L equivalent to 47.72% decrease. However, the first five days were for acclimatization of the microorganisms in the digester during the hydrolysis stage in which the organic matter is being hydrolyzed by enzymes to monomers for enhancing efficient digestion process by microorganisms. That is why, during this stage, the percentage of oxygen (13.8%) was higher than methane (1.1%) and carbondioxide (4.2%) as indicated in Table 6. Nevertheless, the amount of both TS and VS for influent waste during phase I of AD process was higher, specifically the VS, which signifies a high measure of the organic matter. On the other hand, the ratio between VFA and alkalinity is another potential parameter which can be used to evaluate the process stability of the digester. Results in Table 5 show that at day 13, the ratio was 0.54 but decreased to 0.37 in day 37. From day 13 to day 37, it is regarded that both acetogenesis and methanogenesis stages were in the process, by considering the increase of methane content from 46.8% to 69.6% as indicated in Table 6. This suggests that the mixture took 23 days to adapt and develop a methanogenic community. However, the higher content of methane which was obtained at day 37 (69.6%), was characterized by the decrease of VFA concentration about 300.18 mg/L, less VFA/Alkalinity ratio of 0.37, the decline in ammonia nitrogen concentration (NH_3–N) from day 13 to day 30 and optimum pH of 7.51. The increase of VFA concentration in the first 30 days was associated with the total breakdown of organic content and adaptation of methanogens in the digester at the mesophilic temperature. However, the decrease of VFA concentration in the last 30 days as indicated in Table 5 was due to the fact that methanogens were consuming the VFA produced during fermentation process as a substrate to produce methane (Hu *et al.*, 2018). From day 37 to day 44, the decrease in VFA/alkalinity ratio was an essential parameter which indicated that it influences the increase of methane content. For example, both Table 5 and Table 6 shows that in day 37, the maximum methane content was 69.6% at the VFA/Alkalinity ratio of 0.37 which is in line with the recommended threshold value of 0.3 – 0.4 (Zhang *et al.*, 2015). However, a further decrease of methane content in the last 15 days from day 52 to 68 was characterized by less VFA/alkalinity ratio which was below the recommended value and high ammonia content (TAN) as indicated in Fig. 8. This trend though didn't affect the pH of the digester. Still, it indicated that the methanogenesis process was at the end stages, justified by less methane content (24.6%), less effluent concentrations of both chemical oxygen demand (COD) and Biological oxygen demand (BOD) of 1575 and 375 mg/L respectively.

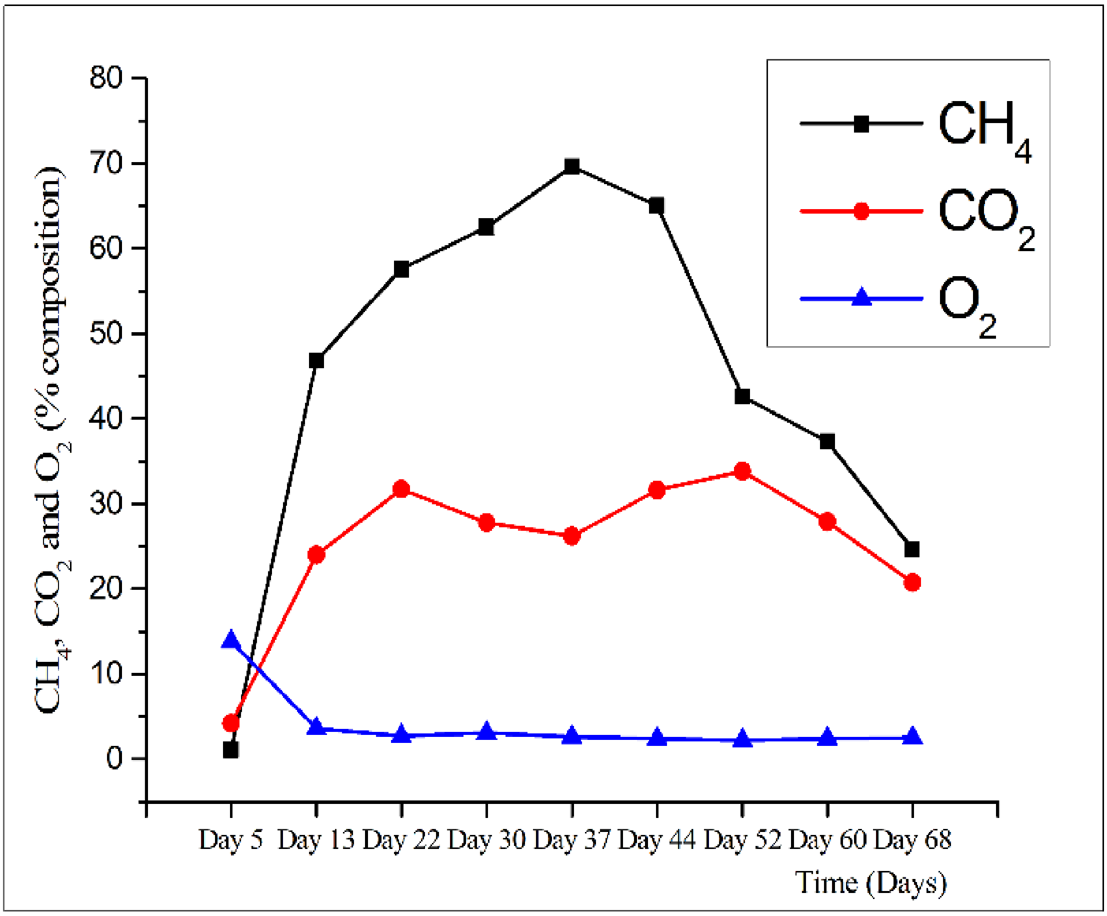

Figure 5: **Percentage composition of methane, carbondioxide and oxygen gases against time**

The increase of VFA in the first 28 days from day 1 to 30, as indicated in Fig. 5, signifies that the acidogenic bacteria are actively working by degrading organic matter into VFA (Ravindranath *et al.,* 2010). However, this process is a significant breakthrough which indicates that the microorganisms can survive during both acidogenesis and methanogenesis stages by utilizing intermediate products such as acetate, butyrate and lactate which are formed before VFA accumulation (Paschal *et al.*, 2017).

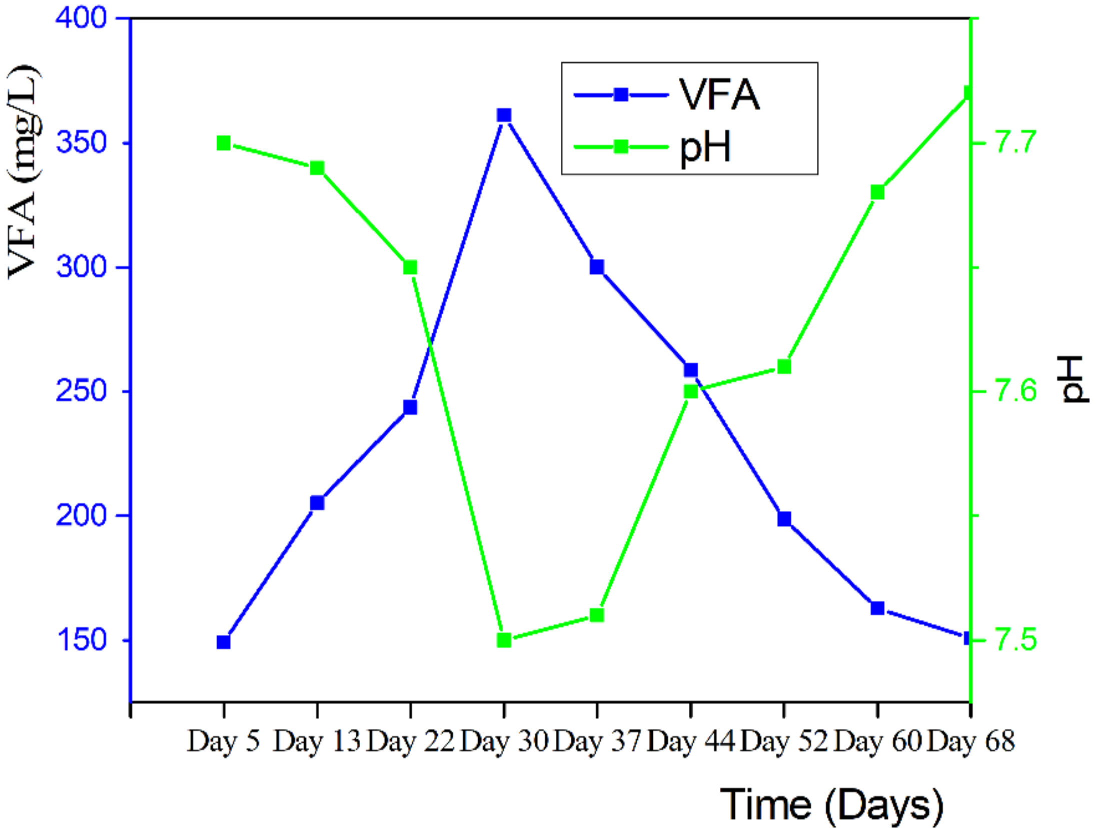

Figure 6: VFA accumulation against time

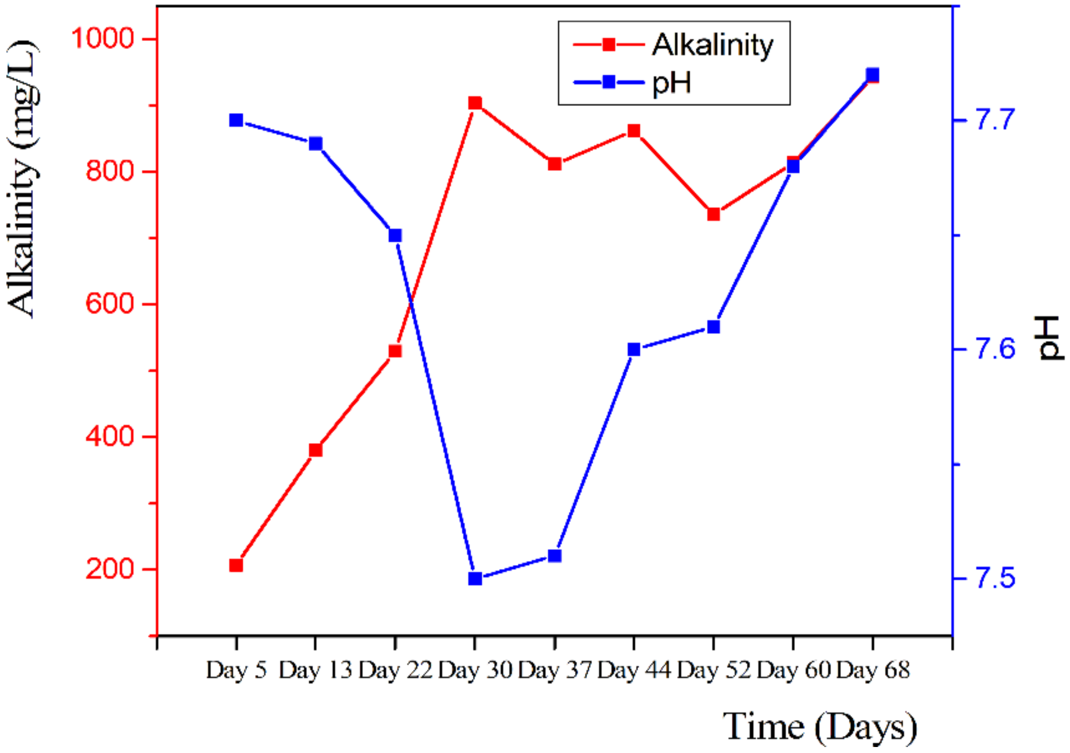

Figure 7: Alkalinity accumulation against time

4.3 Ammonia Inhibition

From results in Table 7, different forms of ammonia such as NH_4^+ and NH_3–N were analyzed in the liquid phase at different interval of time, in which temperature and pH were regarded as controlling parameters. However, the concentrations of all the species were fluctuating since the pH of the waste in the digester was not constant.

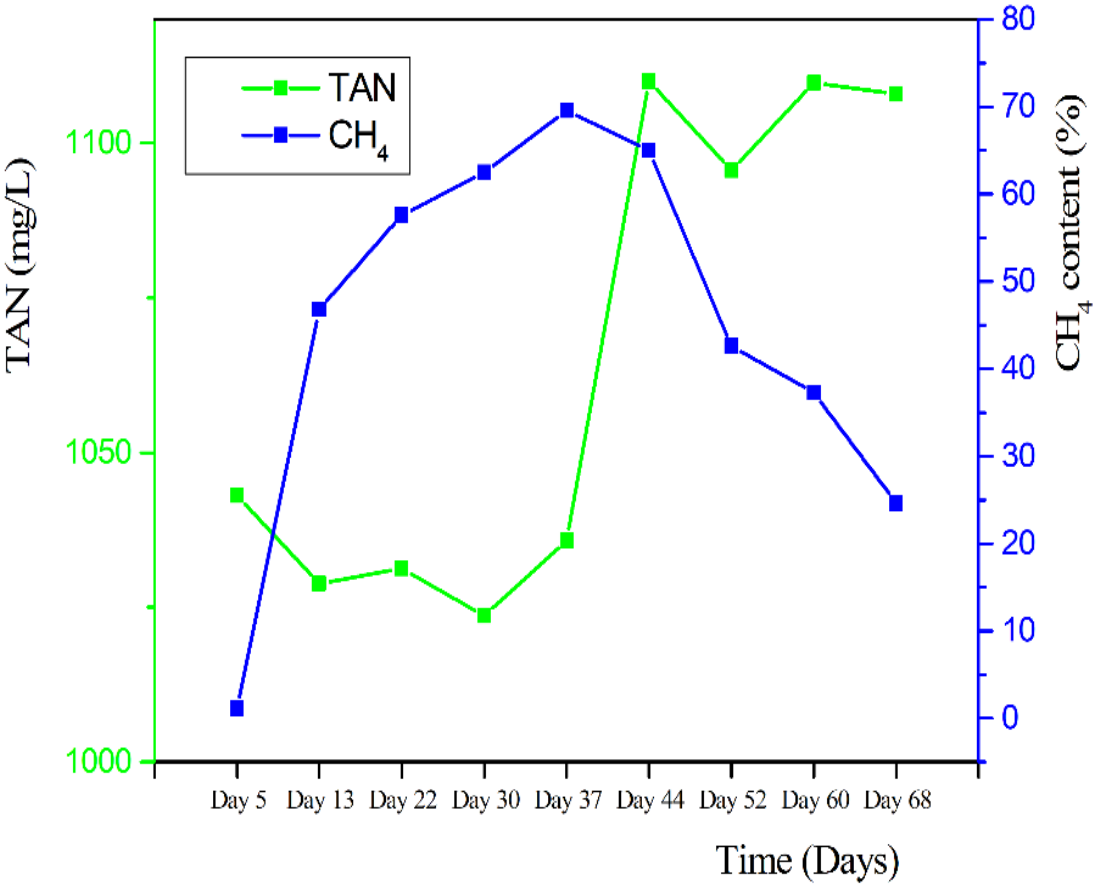

Figure 8: **Accumulation of total ammonia nitrogen (TAN) in relation to methane content against time**

The inhibition process is mostly influenced by the presence of two principal forms of inorganic nitrogen concentrations in the liquid phase (NH_3, and NH_4^+), but dissolved ammonia $(NH_3)_{(aq)}$ is considered as a potential inhibitor due to its high permeability to the bacterial cell wall (Mutegoa *et al.*, 2020; Rajagopal *et al.*, 2013). Since there was an increase in pH of the digester from 7.51 to 7.72 in the last 30 days from day 37 to 68, this condition eventually elevated the level of total ammonia nitrogen (TAN) in the reactor at mesophilic temperature, because of temperature which influences the dissociation constant of dissolved ammonia (Hansen *et al.*, 1998). The increase of TAN as shown in Fig. 8 stimulated the inhibition process, which is indicated by the decrease in methane content.

From results on methane production, Table 7 shows that the methanogenesis stage had acclimatized since day 13 when methane composition was 46.8% though the concentration of TAN was (1028.82 mg/L). However, during day 30, the concentration of TAN decreased to 1023.62 mg/L with a huge increase in methane composition (62.5 %). Considering this trend and results reported in Table 7 and Fig. 8, it is evident that the system performance of the digester attained its methanogenesis stage since day 13 even though the concentration of TAN was at its highest level (1028.82 mg/L) but decreased to 1023.62 mg/L in the day 30. These results have two implications; firstly it indicates that during early stages of anaerobic digestion, some amount of dissolved ammonia is beneficial for bacteria growth since the concentration of dissolved ammonia decreased from 1043.09 mg/L to 1023.62 mg/L in 24 days. Secondly, the results imply that the decrease of inhibition level, which is associated with the decrease of TAN concentration resulted in methane increase by 25.12% from day 13 to day 30. However, there was a high accumulation of TAN from day 37 to day 44, as illustrated in Fig. 8 due to further degradation of the nitrogen-rich protein components from blood mixed with slaughterhouse waste. Also, Fig. 8 illustrates the trend in which methane content decreased as the concentration of TAN was increasing from day 44 to day 68. This trend showed that in the last 23 days, the methanogenesis process was approaching towards completion. Though, the increase in percentage composition of CO_2 from day 37 to 52, as indicated in Fig. 5 was significant for producing bicarbonate ion (HCO_3^-) (Equation 24). This ion acts as a buffer for maintaining process stability and resisting more changes in pH. It is during this stage in which the system was internally buffered, and methane production rate was increased.

The carbondioxide in the digester forms a bicarbonate ion in the liquid phase through a reaction described below (Nysing & Kramers, 1958).

$$\mathrm{CO_2 + OH^- \rightarrow HCO_3^-} \tag{24}$$

Although the much slower reaction may occur:

$$\mathrm{CO_2 + H_2O \rightarrow H_2CO_3} \tag{25}$$

Nevertheless, the process stability and pH was maintained due to less accumulation of volatile fatty acids (VFA) in the digester, but also the performance of the digester can be described by the VFA/Alkalinity ratio which was between 0.3 and 0.4. This ratio is a good indicator which suggests that the function of the digester was good at the beginning and mid of the digestion process (Haider *et al.*, 2015).

4.4 Sulfide Inhibition

The amount of sulfide produced during anaerobic digestion is an indication of sulfate-reducing bacteria (SRB) which reduces sulfates (SO_4^{2-}) present in the waste to sulfide (S^{2-}) which is inhibitory to methanogens. The results indicated in Table 7 show the highest concentration of sulfide (32.60 mg/L), which was obtained during day 5. Similarly, the methane content was 1.1%, indicating that the SRB were outcompeting methane-producing bacteria (MPR) in the first days of anaerobic digestion. However, the decrease in pH from day 13 to 30 resulted into a decrease of sulfide concentration in aqueous solution from 27.0 mg/L to 9.01 mg/L as illustrated in Table 3 and Fig. 9.

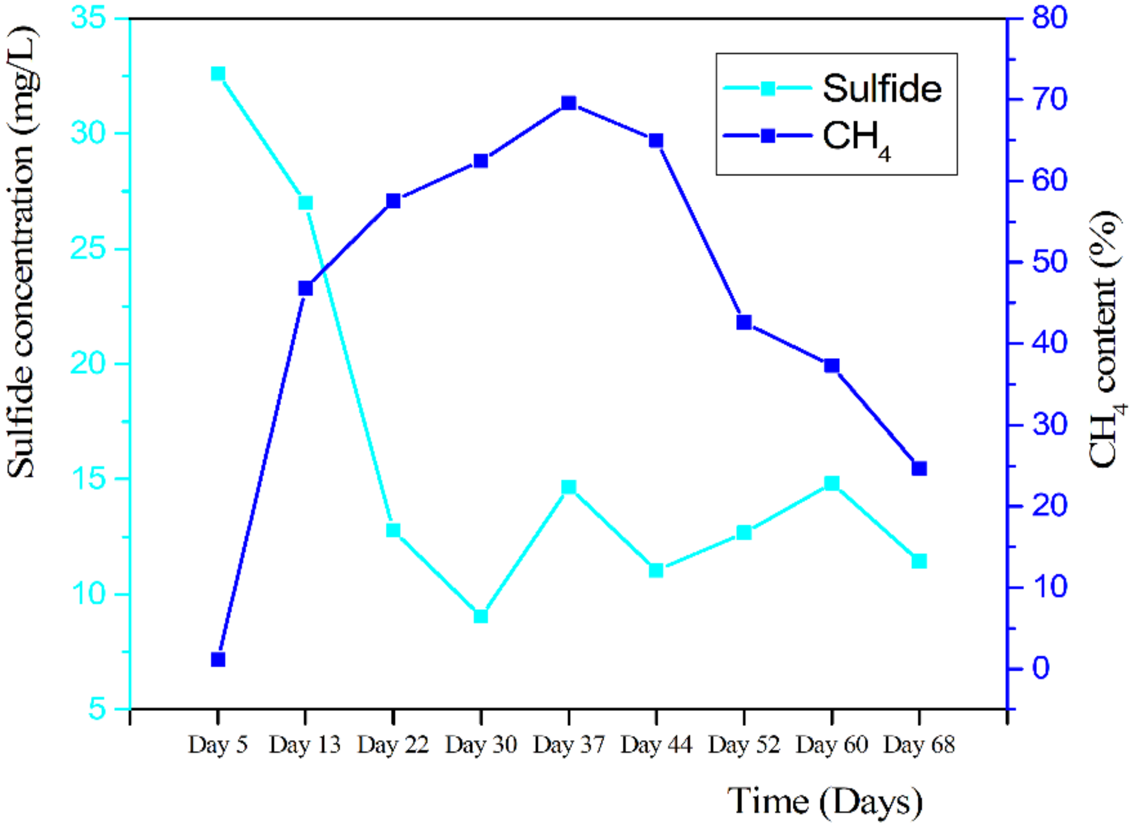

Figure 9: Accumulation of sulfide concentration in relation to methane content against time

These changes also favoured the increase in methane content to 57.6% during day 22 in which the sulfide concentration was reduced to 12.78 mg/L, which is equivalent to 60.79% decrease from day 5. Following the results in Table 6, the concentration of sulfide was decreasing in the aqueous phase but elevated in the gaseous form as hydrogen sulfide (H_2S) in which the amount increased from 12 ppm to 119 ppm from day 5 to day 37.

4.5 Ammonia and Sulfide Interaction

From literature, it has been stated that for stable methanogenesis process, the concentration of H_2S in the liquid phase should not exceed 150 mg/L (Stefanie *et al.*, 1994). In contrast, the concentration of total ammonia nitrogen (TAN) above 1 500 mg/L becomes inhibitory to methanogens (Liu & Sung, 2002). Meanwhile, from the literature of Lauterböck *et al.* (2012), it is revealed that TAN concentration from the digestion of slaughterhouse waste in the range of 1000 – 12000 mg/L can lead to inhibition. This level of inhibition is equivalent to (600 mg NH_4^+-N/L) at 38 °C and pH of 8.1. Therefore, from the experimental results of this study, it is evident that during anaerobic digestion of slaughterhouse waste at mesophilic scale, the inhibition process in the liquid phase was mostly caused by ammonia than sulfide.

4.6 Adsorbent Characterization

4.6.1 X-ray Diffraction Analysis

The XRD analysis was performed in order to ascertain the mineral phases present in both anthill and red rock samples and the profiles for both samples are presented in Fig. 10. From the XRD spectra, it was observed that anthill soil sample (AH) contains quartz (SiO_2), as a dominant phase followed by hematite (Fe_2O_3). In addition to the two major phases, traces of cristobalite (SiO_2) and pyroxene-ideal ($MgSiO_3$) were found to be present. The peaks for quartz appears at 2θ = 25.39°, 32°, and 47.6° corresponding to d = 4.07, 3.25 and 2.22 Å, respectively, while those for hematite appears at 2θ = 28.1°, 38.84° and 41.71° corresponding to d = 3.67, 2.69 and 2.51Å, respectively. The diffraction peaks for trace minerals were identified as follows; cristobalite (2θ = 24.85° and 41.12° for d = 4.16 and 2.55 Å), and pyroxene ideal (2θ = 23.07°, 32°, 36.12°, 41.12° and 47.6° corresponding to d = 4.47, 3.24, 2.88, 2.54 and 2.21 Å, respectively). On the other hand, the XRD profile of red rock soil (RR) confirmed the presence of albite ($Al_{1.02}Ca_{0.02}Na_{0.98}Si_{2.98}O_8$) as the dominant phase followed by pyroxene ($Al_{1.38}Ca_{0.74}Fe_{0.16}Mg_{0.01}Si_{1.5}O_6$), quartz ($SiO_2$), stishovite ($SiO_2$) and hematite ($Fe_2O_3$). Traces of downeyite ($SeO_2$), halite (NaCl), magnetite and witherite ($BaCO_3$) were also observed. The diffraction patterns of the dominant albite phase were observed at 2θ = 25.65°, 27.56°, 28.11°, 29.85°, 31.0°, 32.3°, 34.80°, 35.39°, 38.72°, 40.90°, 41.62°, 47.0°, 49.05° and 52.0° corresponding to d = 4.02, 3.75, 3.68, 3.47, 3.34, 3.21, 2.99, 2.94, 2.69, 2.56, 2.51, 2.24, 2.15, and 2.04 Å, respectively. The pyroxene phase registered its peaks at 2θ = 28.11°, 31.0°, 32.3°, 34.8°, 35.39°, 35.96°, 40.90°, 41.62°, and 47.78° at d = 3.68, 3.34, 3.21, 2.99, 2.94, 2.89, 2.56, 2.51, and 2.20 Å, respectively, while peaks for quartz were found at 2θ = 24.97°, 32.30°, 47.78°, 49.05°, and 52° at d = 4.13, 3.21, 2.20, 2.155, 2.04 Å, correspondingly. The peaks for other phases were also found within the same range of diffraction angle of 2θ = 35.39° and 47° at d = 2.94 and 2.2 4Å (stishovite), 2θ = 28.11°, 38.72°, 41.62° and 47.78° at d = 3.68, 2.69, 2.51 and 2.20 Å (hematite), 2θ = 34.80°, and 40.90° at 2.99 and 2.56 Å (magnetite), 2θ = 27.56°, 28.11°, 38.72°, 47.0°, 47.78°, 49.05° and 52.0° at d = 3.75, 3.68, 2.69, 2.24, 2.20, 2.15, 2.04 Å (witherite), 2θ = 31.0°, 35.39° and 52.0° at d = 3.34, 2.89 and 2.04 Å (halite), and 2θ = 24.97°, 27.56°, 32.30°, 34.80°, 41.62° and 49.05° at d = 4.13, 3.75, 3.21, 2.99, 2.51 and 2.15 Å (downeyite), respectively. The diffraction patterns of the phases present in anthill and red rock soil samples are in agreement with the standard diffraction patterns of the respective phases reported in the literature (Fabrykiewicz *et al.*, 2017; Gualtieri, 2000; Levien *et al.*, 1980; Okui *et al.*, 1998; Peacor, 1973; Ross *et al.*, 1990; Ståhl *et al.*, 1992; Thompson & Downs, 2003).

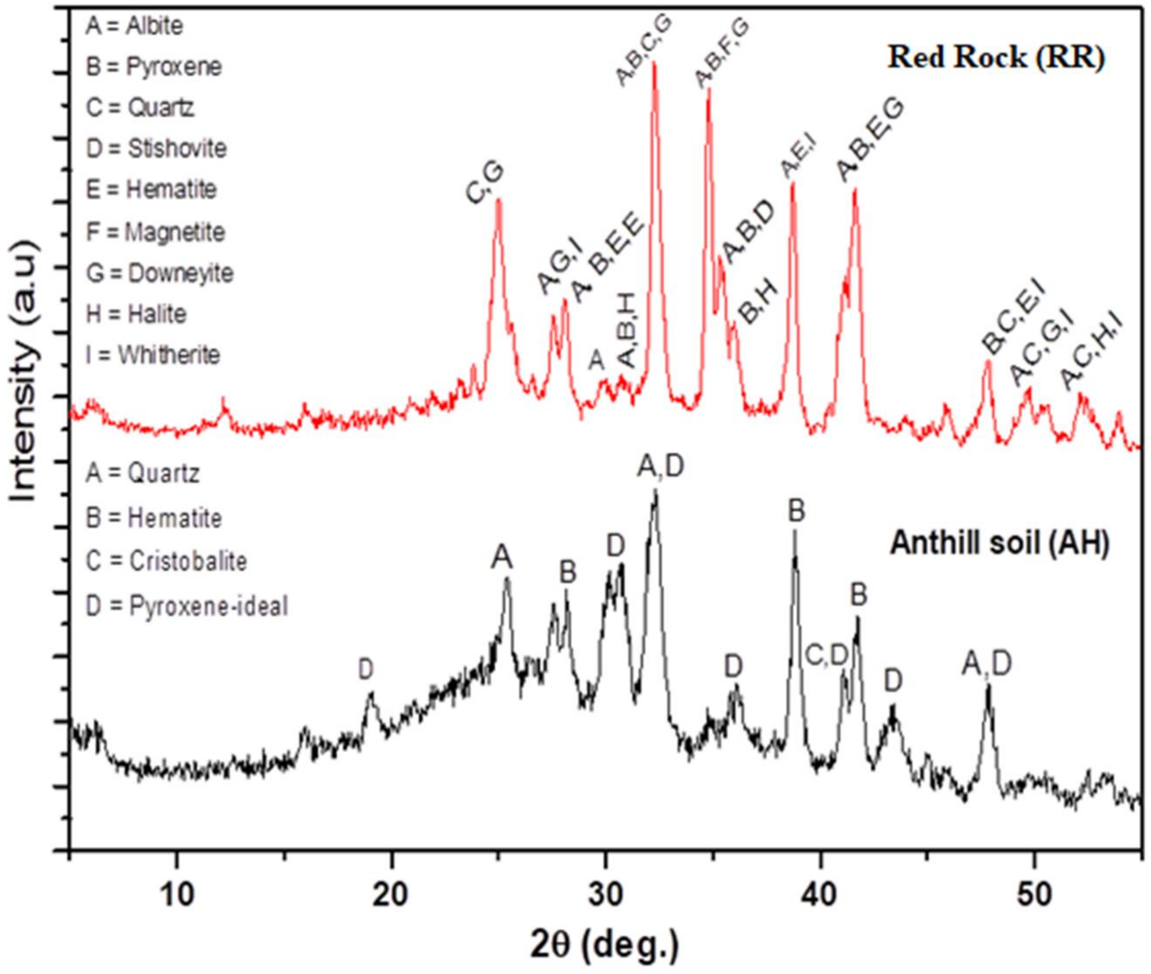

Figure 10: XRD spectra for anthill soil (AH) and red rock soil (RR)

4.6.2 Analysis of Chemical Composition (XRF)

The XRF results of AH and RR samples are displayed in Table 8 It is observed that the anthill soil (AH) has higher amount of Al_2O_3 (36.15%), which is greater than the amount of all other chemical components. In addition, the presence of both Al_2O_3 (36.15%) and SiO_2 (16.83), confirms the aluminosilicate nature of the soil. Similarly, red rock soil (RR) contains high proportions of SiO_2 (31.33%) and Al_2O_3 (23.23%). Since, silica (SiO_2) and alumina (Al_2O_3) are vital components of both soil samples, an elegant mixture of the two soil samples coupled with their synergism is expected to enhance the removal efficiency of pollutants in the substrate undergoing the AD process. Besides, the alumina and silica, both soil samples have an appreciable content of hematite (Fe_2O_3) which a key component for the precipitation of sulfides. Furthermore, the loss on ignition (LOI) which is an index measure of organic content of the soil shows that anthill soil has high amount of volatile content than red rock soil. The LOI for anthill soil is enriched by the build-up of a distinct surface crust during heating that insulates the core of the sample from ignition temperatures (Smith, 2003). Generally, the compositions of the two soil samples in terms of relative weights were found to be in good agreement with the major phases obtained from XRD analysis.

Table 8: Chemical composition of AH and RR analyzed by XRF

Sample ID	SiO_2(%)	CaO(%)	MgO(%)	Fe_2O_3(%)	Al_2O_3(%)	Na_2O(%)	L.O.I
AH	16.83	1.61	1.51	12.14	36.15	-	16.52
RR	31.33	9.54	7.79	14.38	23.23	9.14	4.42

4.6.3 Fourier Transform Infra-Red Analysis

The functional groups of the sorbent materials were analyzed by Fourier Transform Infra-Red Spectroscopy and the results are displayed in Fig. 11. The FT-IR spectra indicate the presence of Si-O- group at the surfaces of both AH and RR materials. Silanol groups (Si−OH) are formed due to the fragmentation of silica surfaces, and are commonly available on the surface of the adsorbent material due to the presence of silica (SiO_2) as reflected in the XRF results (Table 8). In both anthill and red rock soil samples, the broad bands assigned for Si-O- were observed around 1000 cm^{-1}. The other species that may be present on the silica surface is hydrogen-bonded to silanol groups which are significant for enhancing adsorption process through interaction with the adsorbates.

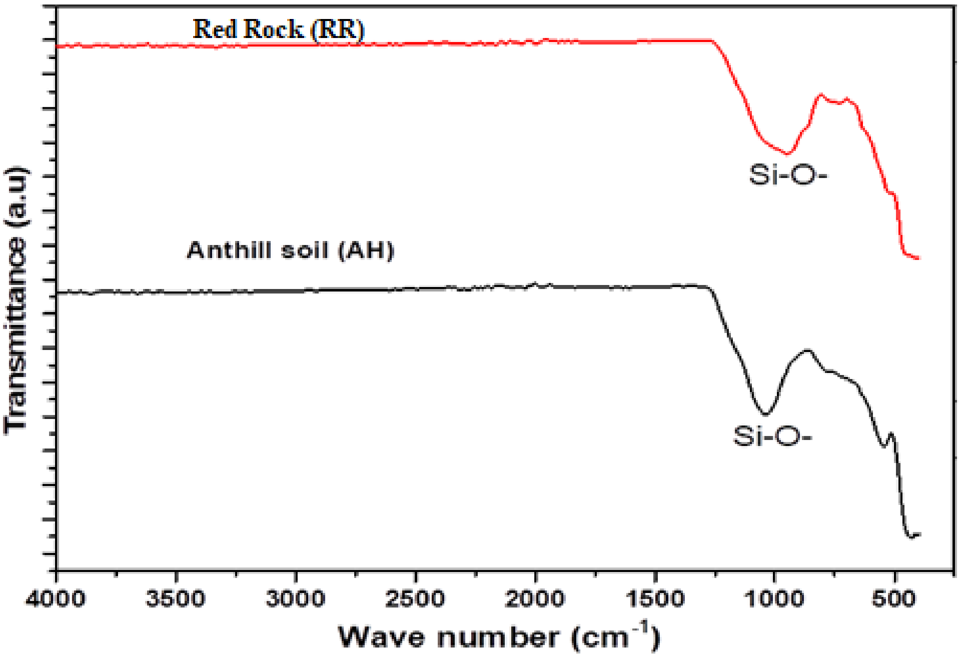

Figure 11: Fourier Transform Infra-Red spectra for Anthill and Red Rock

4.6.4 Analysis of Brunauer-Emmet-Teller Surface area and Porosity Characteristics

The calcination of aluminosilicate materials is essential for volatilization of the organic template and condenses the silanol groups present in the silicate cage. The process enhances the surface area and micropore volume, and exposes the silanol groups at the surface of adsorbent material for improving the adsorption capacity. Results in Table 9 indicate that the surface areas of both anthill and red rock soil samples were obtained at higher calcination temperature. The anthill soil calcined at 700 and 900 °C developed a surface area of 613.88 and 815.35 m^2/g, respectively. Meanwhile, the red rock soil developed a surface area of 601.43 and 852.8 m^2/g at 700 and 900 °C, respectively. Also, the pore volume for anthill soil sample increased from 0.51 cm^3/g at 700 °C to 1.21 cm^3/g at 900 °C. Likewise, the pore volume for red rock soil augmented from 0.62 cm^3/g at 700 °C to 0.75 cm^3/g at 900 °C. Furthermore, the pore diameter for both anthill and red rock soil samples seemed to increase with calcination temperature. For instance, the anthill soil calcined at 700 °C recorded pore diameter of 15.19 Å which increased to 15.22 Å at 900 °C. On the other hand, the pore size of the red rock soil sample increased from 15.17 at 700 to 30.49 Å at 900 °C.

Table 9: Brunauer-Emmet-Teller surface area, pore size and pore volume for AH and RR samples

Parameters	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (Å)
Anthill soil			
AH700	613.88	0.51	15.19
AH900	815.35	1.21	15.22
Red rock soil			
RR700	601.43	0.62	15.17
RR900	852.8	0.75	30.49

The effect of calcination of the adsorbent materials is further manifested by N_2 adsorption-dsorption and micropore development. As a result of calcining anthill soil at 900 °C, it was possible to achieve higher N_2 adsorption with the highest possible pore volume of 816.32 cm^3/g and a relative pressure of 0.99 P/P_0 (Fig. 12b). Similarly, red rock soil calcined at the same temperature attained higher N_2 adsorption with the pore volume of 515.85 cm^3/g at relative pressure of 0.99 P/P_0 (Fig. 12d). This implies that the calcination process favoured the formation of both micropores and mesopores in both adsorbent materials. Since anthill soil exhibited higher N_2 adsorption capacity than red rock soil, it is therefore agreed that anthill soil has higher pore volume and sufficient surface area features than red rock soil. This means that anthill soil has efficient adsorption properties compared to red rock soil.

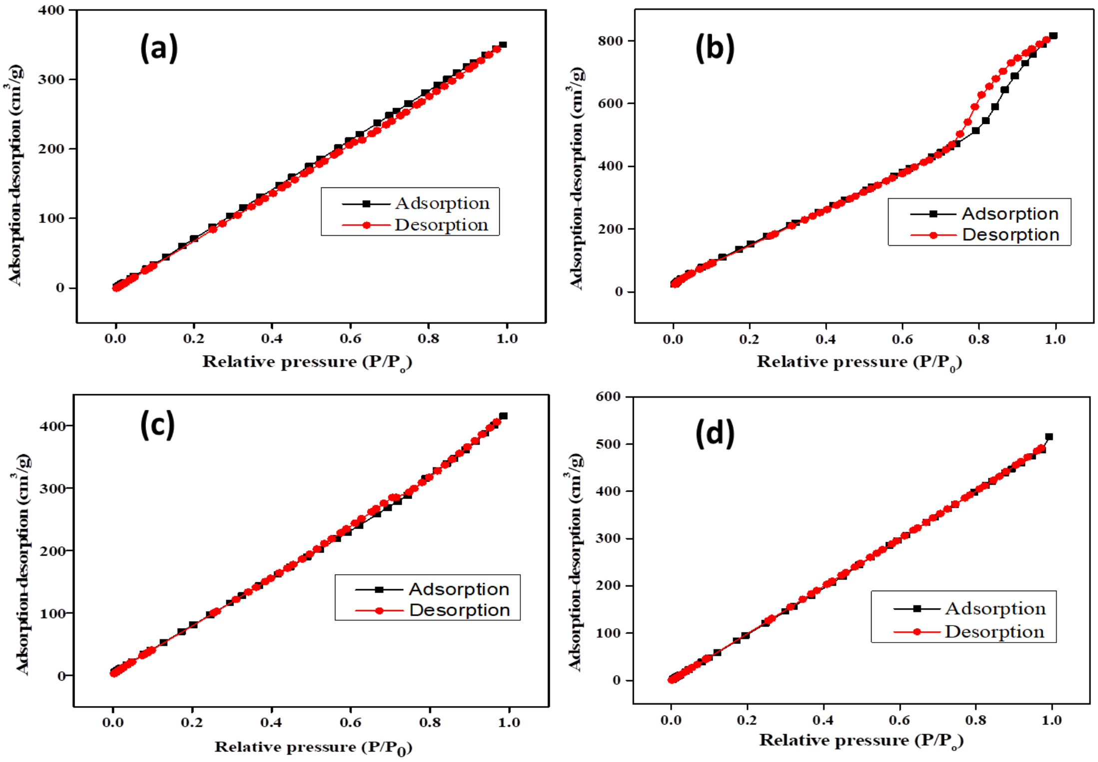

Figure 12: Adsorption-desorption isotherms for (a) AH700 (b) AH900 (c) RR700 (d) RR900

4.6.5 Morphological Analysis

The surface morphology of AH and RR adsorbents calcined at 700°C and 900°C were ascertained by FE-SEM and the micrographs are displayed in Fig. 13. It can be seen that the adsorbent displays small hollow multipores which are likely to contribute to the increase in the surface area. The agglomeration of particles is also obvious in the adsorbent material. The observed agglomeration of the adsorbent materials can be attributed by the magnetic interaction among the hematite/magnetite components of the materials, where each magnetic particle behaves as a magnet (Yeap *et al.*, 2017). The extent of agglomeration is observed to increase with calcination temperature, a phenomenon which enhance high uptake of TAN and sulfide contaminants in the liquid phase.

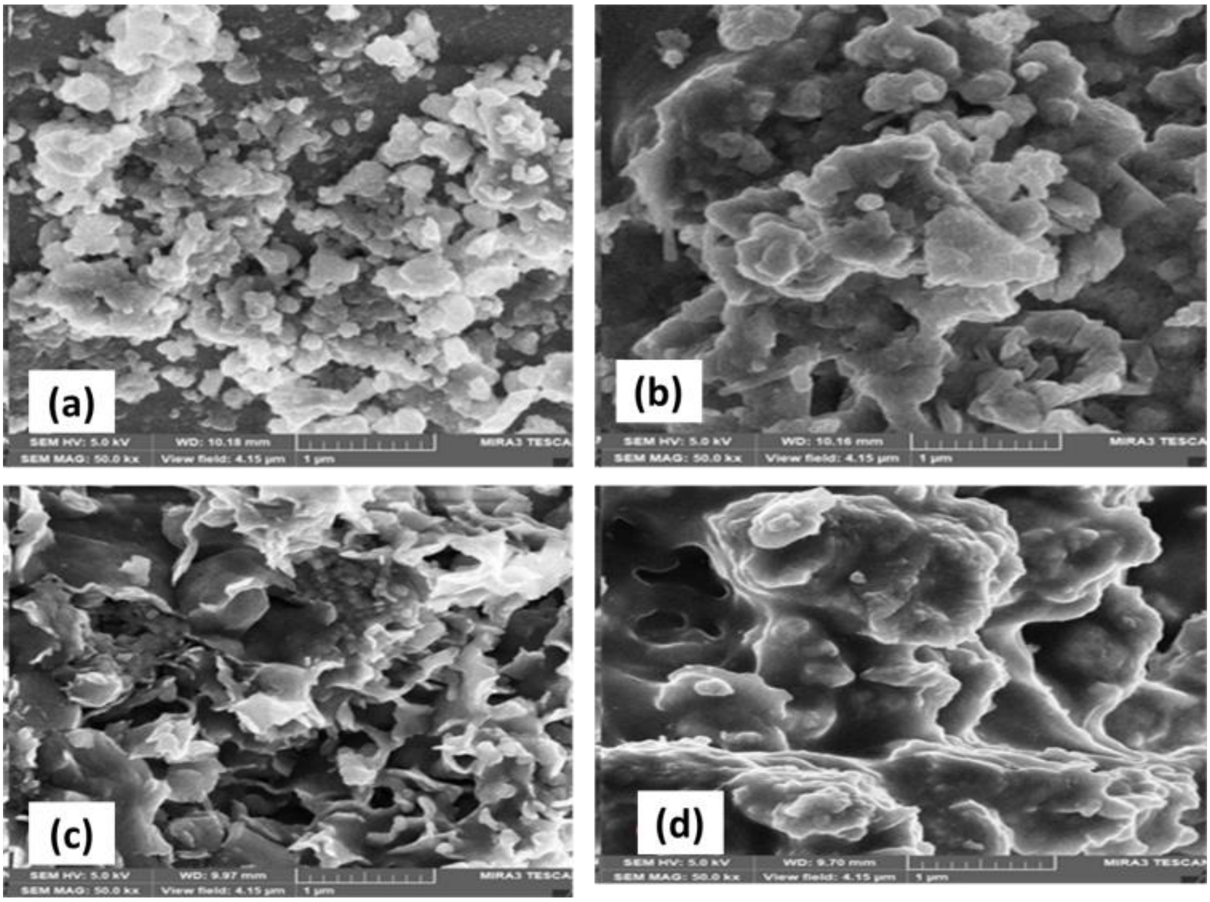

Figure 13: SEM images for (a) AH700 (b) AH900 (c) RR700 (d) RR900

4.7 Determination of Parameter Composition of Slaughterhouse Waste Undergoing Anaerobic Digestion

In the course of anaerobic digestion of slaughterhouse waste different parameters such as VFA, alkalinity, TAN, sulfide, pH and methane were determined in both control experiment and after addition of the adsorbents. From the results in Table 10 notably a control experiment, the TAN level (obtained with the aid of Equation 16) was increasing throughout the digestion process, though there was a decrease in VFAs concentration which is regarded as food for methanogens (Lu *et al.,* 2019). The increasing trend of TAN affected methane production from day 37 to day 44 leading to the decrease in methane content by 35.9%. However, the decrease in methane content was further observed throughout the AD process as the amount of TAN increased. From Table 10, the minimum concentration of TAN was 1022.64±0.95 mg/L recorded in day 22, and increased tremendously as the degradation process was proceeding. The amount of TAN recorded was far above the recommended level for methanogens to resist the inhibition process. This is supported by the fact that TAN concentration in the range of 1000 – 1500 mg/L is often regarded as the key factor for inhibition and AD failure in general (Capson-Tojo *et al.,* 2020). This indicates that the methanogenesis stage was highly affected due to inhibition process attributed by a higher concentration of TAN. The ratio between VFA and alkalinity can be considered as an essential parameter to describe the digester's performance at mesophilic temperature. Since VFA is regarded as food for methanogens during fermentation (Hu *et al.,* 2018), its decrease is associated with the total breakdown of organic content by microorganisms. However, the VFA/alkalinity ratio produced between day 26 (0.39) and day 44 (0.31) is within the recommended threshold value of 0.3 – 0.4 (Zhang *et al.,* 2015), for a stable biodigester with a pH range of 7.5 – 7.6. For instance, the highest methane content of about 55.7% was recorded during day 37 in which the VFA/alkalinity ratio was 0.34 as indicated in Table 10. Nevertheless, from day 37 onwards, the control experiment showed the decrease in the threshold value as the TAN concentration was increasing. This phenomenon coupled with the inhibition process induced by high accumulation of TAN concentration, resulted into the decrease of methane content.

Table 10: Parameter analysis of slaughterhouse waste before and after adsorption during the Anaerobi Digestion process

	Control Experiment							**Parameters assessed after addition of adsorbents**		
	VFA (mg/L)	**Alkalinity (mg/L)**	**Ratio (VFA/Alk)**	**TAN (mg/L)**	**S^{2-}(mg/L)**	**%CH_4**	**pH**	**VFA**	**%CH_4**	**pH**
Day 1(in)	152.89±2.22	202.23±3.25	0.76	1041.03±2.59	32.54±0.59	-	7.70			
Day 8	210.5±2.1	285.32±4.71	0.74	1029.38±2.38	27.20±0.66	29.2	7.69			
Day 15	270.45±0.70	495.73±5.49	0.55	1030.04±1.05	13.41±0.74	41.2	7.65			
Day 22	390.85±5.94	819.77±3.53	0.48	1022.64±0.95	9.610±1.04	54.3	7.50			
Day 26	304.51±6.16	786.99±4.83	0.39	1035.79±1.56	14.51±0.64	52.8	7.51			
Day 37	274.41±7.39	804.24±5.81	0.34	1093.81±2.78	10.51±0.45	55.7	7.42			
Day 44	216.31±4.85	811.59±2.48	0.31	1111.91±1.53	12.41±0.35	35.7	7.24			
Day 51	173.16±2.36	821.56±4.15	0.21	1109.43±1.09	14.93±0.15	28.2	7.18	152.24	41.0	7.31
Day 58	142.48±3.5	847.96±4.91	0.17	1109.79±1.95	11.31±0.06	24.6	7.06	122.54	48.4	7.42
Day 65	135.09±2.43	938.74±4.47	0.14	1210.17±0.71	10.28±0.24	22.8	7.10	112.82	60.3	7.50

4.8 Adsorption of Total Amonia Nitrogrn and Sulfide by Anti Hill @ Red Rock Adsorbent

4.8.1 Determination of Adsorption Capacity (mg/g) and Removal Efficiency (%)

The removal efficiency of both TAN and sulfide in the liquid phase was estimated using Equation 18 based on the mixing ratios of anthill and red rock adsorbents. The AH to RR adsorbent ratios were 1:1, 1:2 and 3:1 for TAN adsorption and 1:1 and 1:2 for sulfide adsorption. From the results indicated in Fig. 14(a), it is clear that the removal efficiency for TAN showed a clear order basing on calcination temperature since the adsorbent mixtures calcined at a temperature of 700 ℃ had better removal efficiencies than those at 900 ℃ for all ratios. However, for sulfide (Fig. 14(b) the effect of calcination temperature was insignificant while there was clearly a strong dependency on the ratios. In addition, the higher sulfide removal efficiency demonstrated by the adsorbent ratio of 1:2 is ascribed to the appreciable content of hematite (Fe_2O_3), which influenced the precipitation reaction of iron sulfide. Moreover, the higher mixing ratio of red rock soil sample seemed to perform better in removing sulfide in the liquid phase with almost 80% removal efficiency. The results of this study are comparably higher or within the range of previous studies on other adsorbents in removing TAN and sulfide in the liquid phase (Dar *et al.,* 2015; Zhu *et al.,* 2012). Nevertheless, the frequent use of ferric and ferrous salts (Fe^{3+}/Fe^{2+}) which oxidizes sulfur has been commonly practised in which the combined species has depicted higher removal efficiency of sulfide in the aqueous phase than when either of the species is used alone (Firer *et al.,* 2008). Farghali and other co-authors have indicated that the reduction of hydrogen sulfide (H_2S) can be achieved in the range of 83.82 – 98.10% from day 10 during AD of cattle manure through direct application of metal oxide nanoparticles (Farghali *et al.,* 2019). The present study, however, has demonstrated the use of local powder processed from cheaply and abundant inorganic materials collected from Northern zone of Tanzania, for the removal of ammonia and sulfide in the liquid phase.

In addition to the removal efficiency (%), the adsorption capacity (mg/g) of different ratios of adsorbent mixture was determined with the aid of Equation 17, and the results are presented in Fig. 15.

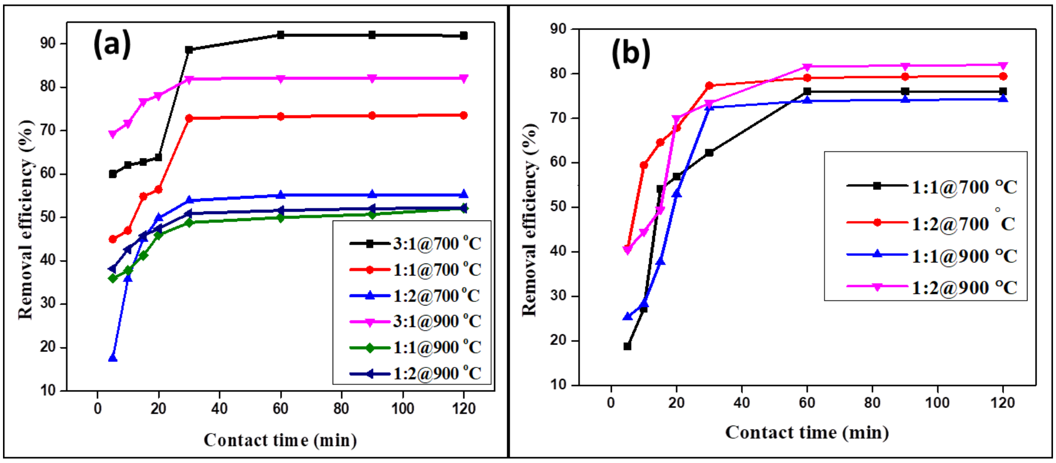

Figure 14: Removal efficiency of (a) Total Amonia Nitrogen and (b) Sulfide at different ratios of adsorbent mixture calcined at 700 and 900 °C

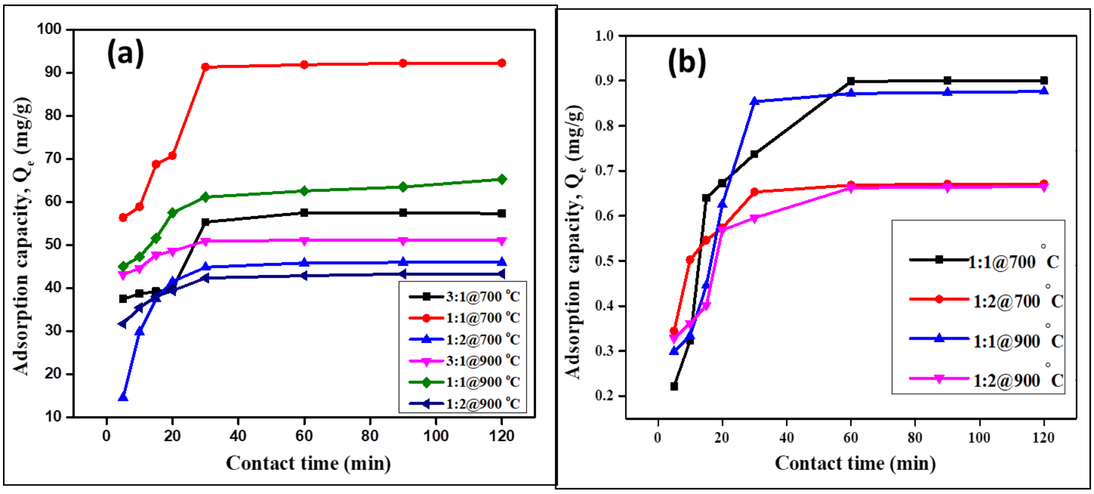

Figure 15: Adsorption capacity of: (a) Total Amonia Nitrogen and (b) Sulfide at different ratios of adsorbent mixture calcined at different temperatures

Figure 15a shows a clear dependency of adsorption capacity of TAN on the calcination temperature at any ratio. At any ratio calcination temperature of 700 ℃ was superior to 900 ℃. Accordingly, the highest adsorption capacity of TAN was achieved at the ratio of 1:1 for the adsorbent mixture calcined at 700 ℃. Nevertheless, a different case has been observed when the adsorption capacity of sulfide is considered. From Fig. 15b, it is clear that the calcination temperature did not significantly influence the adsorption capacity of sulfide at any ratio of the adsorbent mixtures. The highest adsorption capacity of sulfide happened at the mixing ratio 1:1 for both calcination temperatures, while ratio while 1:2 showed much lower sulfide adsorption capacity for both calcination temperatures. From these results, it can therefore be concluded that the mixing ratio of 1:1 and calcination temperature of 700 ℃ produced the highest adsorption capacities of both TAN and sulfide. Similar observations have been reported for most of the adsorbents calcined at the temperature ranging from 500 to 700 ℃, showing high adsorption capacities (Mohan *et al.*, 2014).

4.8.2 Effect of Adsorption Time on the Removal Efficiency

The contact time between the adsorbent and adsorbate is important in determining the adsorption equilibrium. In this study, the removal efficiency of AH@RR adsorbent was studied by varying the adsorption time from 0 to 120 min. As seen from Fig. 14a, all the ratio mixtures have shown maximum removal efficiency of TAN within the first 30 minutes, thereafter little changes on the removal efficiency were recorded, followed by a steady adsorption process. On the other hand, the maximum removal of sulfide was attained during the first 60 min after which constant adsorption process was observed (Fig. 14b). This implies that the adsorption equilibrium was attained during the first 30 min for TAN and 60 min for sulfide under the given conditions and maximum removal efficiency had taken place. This fast adsorption process may be ascribed by fast migration of adsorbate molecules resulting from abundant active adsorption sites on the surface of AH@RR. After equilibrium, the observed steady adsorption is related to the buildup of adsorbate molecules on the adsorbent surface, hence blocking further adsorption of extra molecules to the existing active sites. There are reports on the use of other adsorbent materials in removing TAN and sulfide from environmental matrices. However, most of these adsorbents took longer contact time to reach equilibrium compared to the mixture of adsorbents used in this study. This variation of contact time is attributed to differences in particle size, experimental conditions and surface properties of the sorbent materials. For instance, the study by Njoroge and Mwamachi (2004) revealed that the natural zeolite could even take more than 120 minutes for the uptake of ammonia with the removal efficiency of 50%. Sébastien Ryskie and colleagues (Ryskie *et al.,* 2020) used the ozone microbubbles to evaluate their performance in removing ammonia nitrogen (NH_3-N) in a batch mode. In their study, the removal efficiency in the range of 27.8 – 99.3% was recorded after a treatment period of 570 min. The results on the variation of adsorption efficiency as a function of contact time obtained in this study is a major breakthrough for industrial application because fine adsorbent particles like powdered AH@RR tend to equilibrate with sorbate particles at a very shorter time.

4.8.3 Adsorption Isotherm Studies

Langmuir, Freundlich and Jovanovich isotherm models were studied to evaluate the interaction behaviour between active sites of AH:RR surfaces and the adsorbate particles. These isotherm models provide the correlation between the equilibrium amount of TAN and sulfide in the liquid phase and that in the adsorbent phase. The Langmuir isotherm parameters summarized in Table 11 were computed by using equations 19 and 20 to give the plots shown in Fig. 16a and b. The slope and intercept of the linearized Langmuir plots of C_e/q_e vs C_e were used to obtain the values of q_m, K_L, R_L, and R^2. The feasibility of adsorption was inferred by the values of the separation factor, R_L (Eq. 20). Technically, if $R_L = 1$ (linear adsorption), $0<R_L<1$ (favorable adsorption) and $R_L >1$ (unfavorable adsorption) (Baskaralingam *et al.*, 2006). The values of R_L for the removal of adsorbates were obtained in the range of -0.03 to -0.82 for TAN and -0.13 to -0.31 for sulfide. Since these values do not conform to the relation $0 < R_L < 1$, then it can be deduced that the uptake of both TAN and sulfide on AH@RR was not limited to a monolayer adsorption process, and that the adsorption energy is not uniform for all sites. Hence, based on the values of R_L and the lower regression coefficients, it can be deduced that Langmuir isotherm model cannot conveniently describe the adsorption of TAN and sulfide on the adsorbent used in this study.

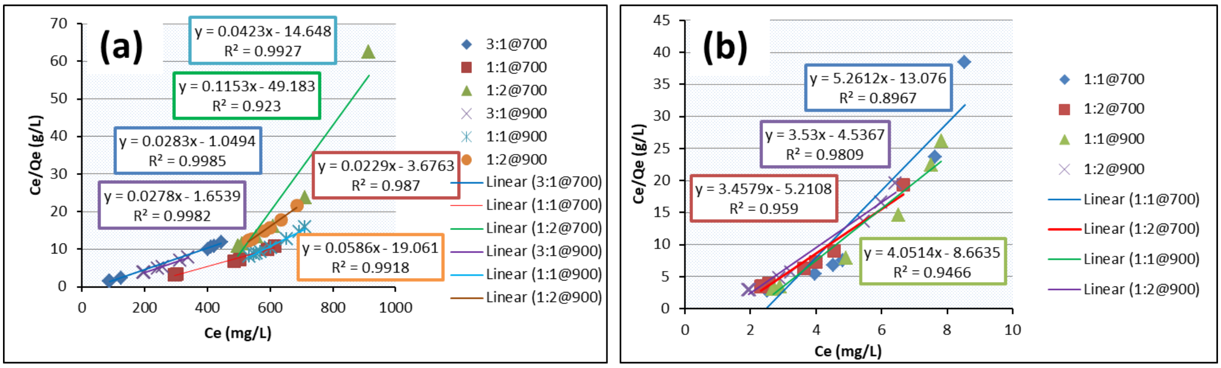

Figure 16: Langmuir plots for (a) TAN and (b) Sulfide removal

Freundlich adsorption model (Equation 21 and 22) is valid for multilayer adsorption processes occurring due to heterogeneity of the system. The linearized plots of log Q_e vs log C_e shown in Fig. 17 were utilized to determine the values of parameters K_F and n (Table 11), which provide insight into the degree of adsorption and heterogeneity, respectively. The model also provides information about the degree of nonlinearity between adsorption and solution concentration. According to this model, the process is favourable if $1< n < 10$, but in cases when n = 1 and n <

1, it signifies linear and slow sorption processes, respectively (Afroze & Sen, 2018). The values of n obtained from this study were found to be less than 1, suggesting a slow uptake of TAN and sulfide from the liquid phase. Also, Freundlich isotherm does not predict the saturation of TAN and sulfide molecules on the surface of adsorbent and thus reinforces the infinite coverage of the adsorbent surface (Karapinar & Donat, 2009). Therefore, it is reasonable to deduce that the Freundlich model was not convenient to recount the adsorption of the two adsorbates.

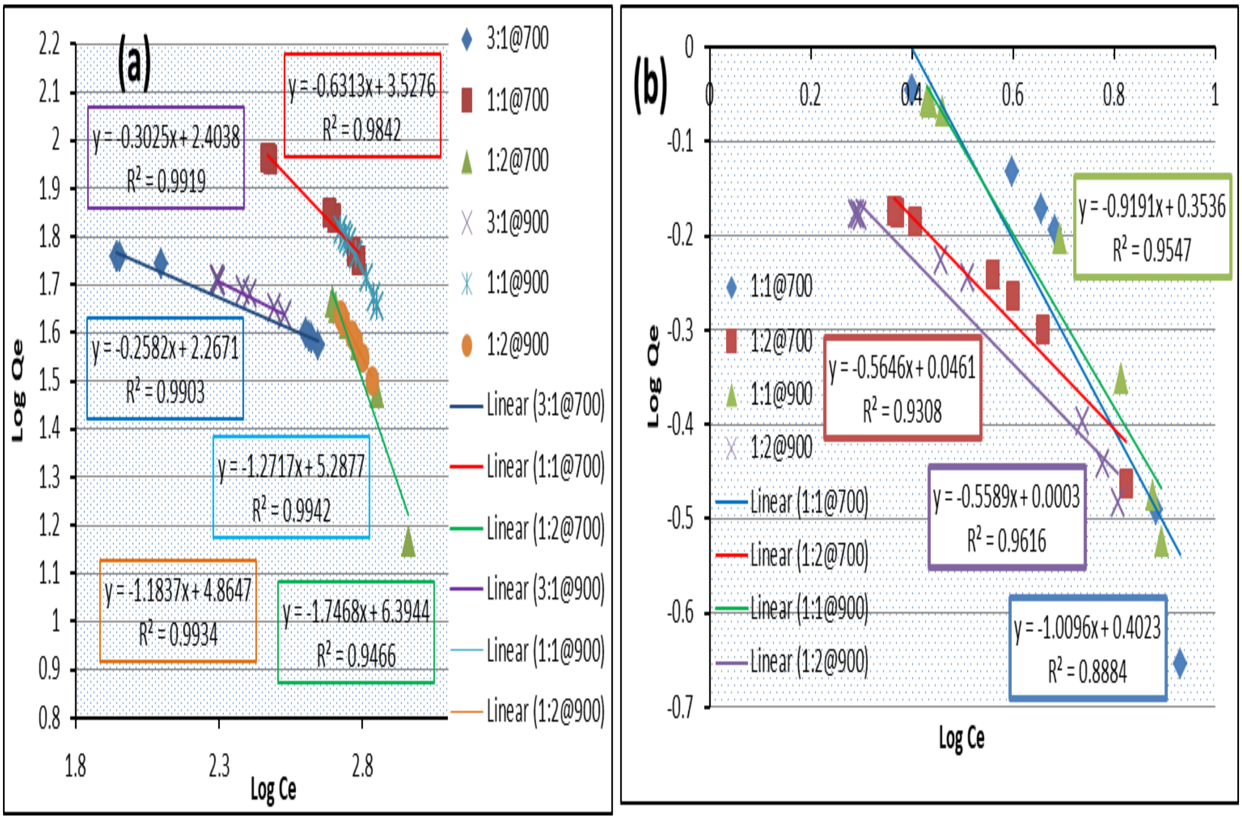

Figure 17: Freundlich plots for (a) TAN and (b) Sulfide removal

To further deduce the model fit to the experimental data, Jovanovich adsorption model was tested and the results are summarized in Table 11 Plots of In Q_e vs C_e were employed to obtain the isotherm parameters using equation 23. The data from Jovanovich adsorption model seemed to fit better than all other models tested, since the Jovanovich constant was in the favourable range of $0 < K_J < 1$ (Khan *et al.*, 2015). The fitting of this model was possible due to the existence of mechanical contacts between the adsorbent and adsorbate. This phenomenon is predisposed by the presence of carboxyl, hydroxyl and amine groups derived from protein molecules present in the slaughterhouse waste (Aly-Eldeen *et al.*, 2018; Panahi *et al.*, 2008). The regression coefficients (R^2) of Jovanovich model were very close to unity, ranging from 0.975 to 0.999, which were higher compared to the regression coefficients obtained from Langmuir and Freundlich isotherms. It is apparent from our findings that the maximum adsorption capacities (qm, (mg/g)) for Jovanovich model (Table 11) are higher than those obtained from Langmuir isotherms, making it more appropriate to adequately describe the adsorption of the TAN and sulfide.

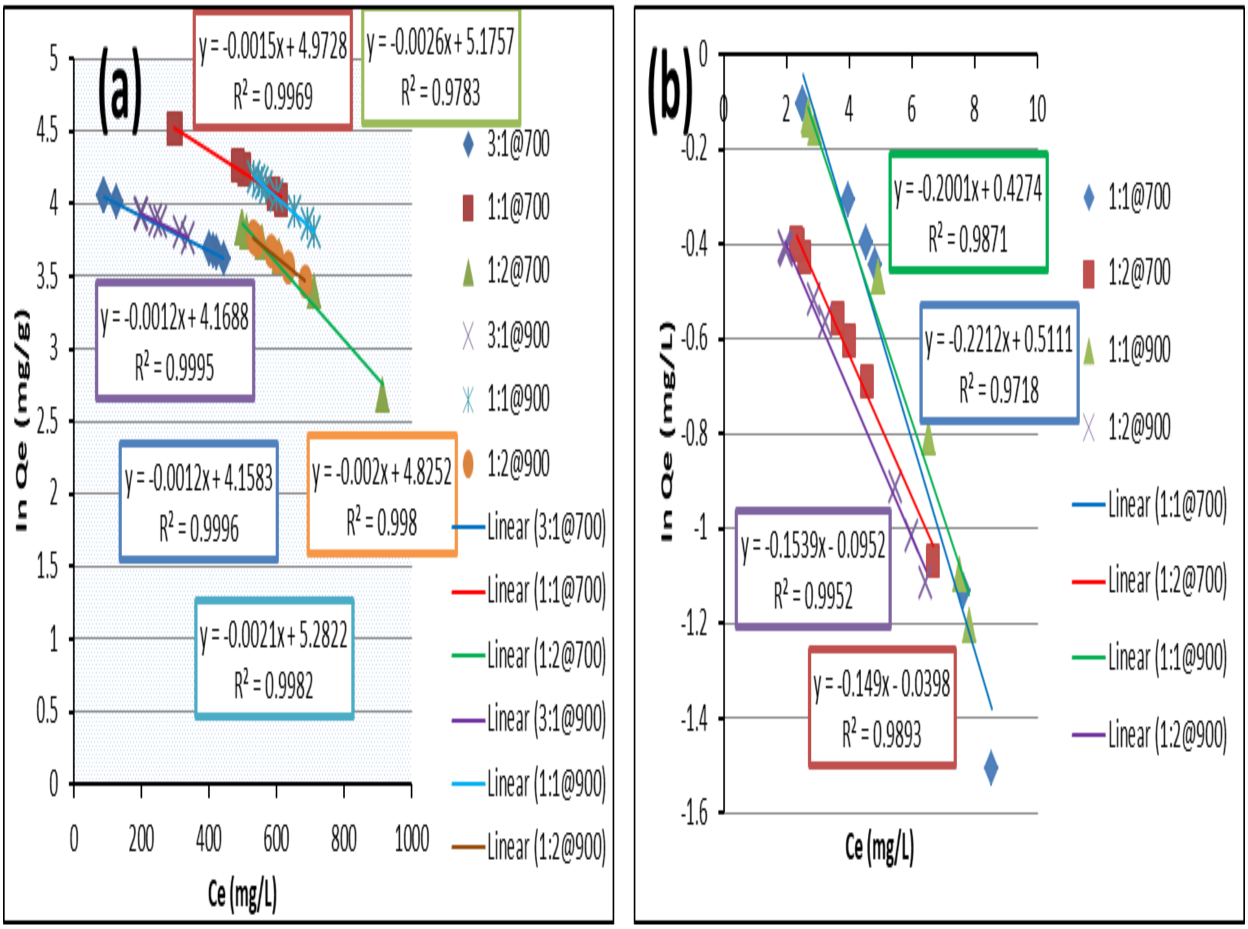

Figure 18: Jovanovich isotherms for (a) TAN and (b) Sulfide removal

Table 11: Summarized isotherm parameters for the adsorption of TAN and sulfide onto AH@RR adsorbent

	Isotherm parameters for TAN						Isotherm parameters for Sulfide			
Temperature	700 ℃			900 ℃			700 ℃		900 ℃	
Adsorbent ratio (AH:RR)	3:1	1:1	1:2	3:1	1:1	1:2	1:1	1:2	1:1	1:2
Langmuir model										
q_m (mg/g)	35.34	43.70	8.67	35.99	23.65	17.05	0.19	0.29	0.25	0.28
k_L (L/mg)	-0.03	-0.006	-0.002	-0.02	-0.002	-0.003	-0.40	-0.66	-0.46	-0.79
R_L	-0.03	-0.18	-0.82	-0.05	-0.82	-0.43	-0.31	-0.16	-0.26	-0.13
R^2	0.998	0.985	0.910	0.998	0.991	0.990	0.897	0.952	0.938	0.978
Freundlich model										
$k_F[(mg/g)(L/mg)^{1/n}]$	184.98	3370	2×10^6	253.39	194×10^3	72×10^3	2.53	1.11	2.26	1.00
n	-3.87	-1.58	-0.57	-3.31	-0.79	-0.84	-0.99	-1.77	-1.09	-1.79
R^2	0.989	0.982	0.938	0.991	0.993	0.992	0.869	0.919	0.947	0.955
Jovanovich model										
q_m (mg/g)	63.96	144.44	179.93	64.64	196.80	124.62	1.67	0.96	1.53	0.91
K_J (L/g)	0.0012	0.0015	0.0026	0.0012	0.0021	0.0019	0.221	0.149	0.20	0.154
R^2	0.999	0.996	0.975	0.999	0.998	0.998	0.967	0.988	0.985	0.994

4.9 The Effect of Inorganic Additives on Methanogenesis

The effect of the adsorbent mixture in the reactor was evaluated in relation to the content of the biogas produced in the next (14) days after the addition of inorganic materials for adsorption process. The adsorption process was done on day 44 after a tremendous decrease in the methane content by 36% from day 37. The effect of the added inorganic materials on methane production was assessed in which the reactor with additive mixture in a ratio of 1:2 showed an increase in methane content by 13 % in seven days (day 44 - 51) from 35.7 to 41.0% of methane content as indicated in Table 10 The trend was different from methane content recorded in the control reactors in which there was a decrease in methane content from day 44 to 65. For instance, in reactor A which was used as a control experiment (no adsorbent mixture was added), 24.6% of methane was produced on day 58 as opposed to 48.4% of methane content produced in reactor B. The trend further showed that the amount of methane in reactor B increased to 60.3% during day 65, while in control reactor A, 22.8% of methane content was recorded on the same day. However, the results were run in triplicate by considering %CH_4 produced in relation to the control reactor. Statistical analysis revealed that the results were more reliable (*P* = 0.001), hence statistically significant.

Generally, the growth of methanogens in the AD system is highly influenced by trace elements such as Fe, Ni and Co (Zhang *et al.*, 2003). Therefore, the application of additives rich in iron such as iron oxides, ferric salts, and other iron-based materials is considered as the best way to improve methanogenesis process to its perfection and increase of methane content (Wang *et al.,* 2018). It is evident that the increase in methane content in this study was influenced by hematite (Fe_2O_3) present in the adsorbent mixture, which has the tendency of enhancing methanogenesis. The process is reinforced by ferric iron from hematite/magnetite present in the mixture of adsorbents which is regarded as an electron acceptor and further oxidizes various organic substances through direct interspecies electron transfer (DIET) from iron oxides (Kim *et al.*, 2014). This process is augmented by the exchange of electrons between fermenters and methanogens, which triggers the rapid degradation of organic matter (Wang *et al.*, 2018). However, the addition of ferrous material during day 44 was a very crucial approach as it accelerated the increase of pH in the reactor from 7.24 (day 44) to 7.50 (day 65) as shown in Table 10 This condition resulted in mitigating the increase of volatile fatty acids and other intermediate products which could further lead into severe stress of methanogens in the reactor, hence low methane content.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This study revealed that the inhibition process was induced by total ammonia nitrogen (TAN) and sulfide level was not a problem during AD of slaughterhouse waste. The lower level of sulfide might have been attributed by iron present in the blood mixed with the substrate, which tends to precipitate sulfur to iron sulfide.

This research has demonstrated that when slaughterhouse waste is treated as a substrate during the AD process, the digester performance can maintain the methanogenesis stage even at the high TAN level. For example, when TAN concentration was 1110.08 mg/L during phase I of AD process, methane composition was 65% at a pH of 7.6. However, in the other study in which methane production pathways at mesophilic temperature were analyzed by comparing with the TAN concentration in a range of 0.14 – 9 g/L, it was observed that 200 mg/L of TAN concentration affected methane production pathways as a result of total inhibition (Hao *et al.*, 2017).

In this study, it is evident that slaughterhouse waste can resist the inhibition process at a high TAN level by increased methane production. This is due to the fact that the pH of the substrate did not drop below 7 throughout the AD process, a condition that could lead to severe stress for microorganisms in the reactor. In addition, this phenomenon can be regarded as a major breakthrough for biogas production using slaughterhouse waste since it doesn’t require any buffering agent. Generally, the pH range between 7 – 8.2 is regarded as an average range for increasing methane production and tolerant to ammonia inhibition (Park *et al.*, 2018).

Nevertheless, a high amount of sulfide accumulation in the first days is a sole indicator that sulfur-reducing bacteria (SRB) were very active in the first days because sulfate reducers tend to outcompete methane-producing bacteria (MPB) by oxidizing molecular hydrogen when COD value is high. Despite the fact that competition between SRB and MPB can bring about inhibition process which lower the percentage composition of methane, ammonia and sulfide concentrations are mostly considered as inhibitory parameters in the liquid phase as a result of protein degradation during anaerobic digestion.

On the other hand, phase II of the AD process investigated the effect of mixing ratios of powdered adsorbent materials processed from anthill and red rock soil samples in removing ammonia and sulfide in the liquid phase during AD of slaughterhouse waste. Analysis of the adsorbent's physicochemical characteristics was performed by p-XRD, FT-IR, porosimeter and FE-SEM techniques. The highest surface area (852.8 m^2/g) and pore volume (0.75 cm^3/g) were displayed by red rock soil sample calcined at 900 ℃. Among all the adsorbent ratios investigated, the ratio of 1:1 and calcination temperature of 700℃ produced the highest adsorption capacities of both TAN and sulfide.

Besides experimental parameters, the high removal efficiency of TAN was attributed to the presence of silanol groups on the adsorbent surfaces, which induce the adsorption of TAN. On the other hand, the efficient removal of sulfide was ascribed to the high content of iron oxide, which precipitates sulfur in the liquid phase. Analysis of adsorption isotherm models demonstrated that Jovanovich model fitted better than Langmuir and Freundlich models, with Jovanovich constant in the range of $0 < K_J < 1$.

Moreover, the adsorbent materials used in this study have been proven to be very potential additives in sustaining the methanogenesis process. After day 44 in which these adsorbents were added, the internal buffer of the reacting system was stabilized by adjusting the pH at the level in which the VFA was decreasing, a condition that alleviated the inhibitory effects of TAN on methane production. Therefore, the addition of inorganic additives rich in iron is generally considered as an appropriate mechanism for controlling inhibition and stimulate the methanogenesis process, which increases methane production.

Therefore, on the basis of these findings, it can reasonably be concluded that anthill and red rock soils can be employed as an affordable and effective adsorbent in remediation of TAN and sulfide in the liquid phase as well as sustaining methanogenesis process.

5.2 Recommendations

Based on the findings in this study, the following are recommended as the follow-up studies to enrich what has been reported here;

(i) This study ascertained the process stability and digester’s performance configured at a mesophilic temperature only. In order to make a reasonable comparison on the performance of the digester at different ranges of temperature, we are highly recommending an assessment of ammonia and sulfide inhibition for the slaughterhouse waste treated anaerobically under both mesophilic and thermophilic temperature scales.

(ii) The inorganic additives which were employed for the removal process of both TAN and sulfide concentrations in the liquid phase were not recycled; instead, they were discharged out from the digester with the effluent. In order to minimize the operational cost of the adsorbent materials during fabrication, we recommend a regeneration process of the materials used which will enable assessing the feasibility of recycling the materials for reuse before getting saturated.

(iii) Since anaerobic digestion involves four stages (hydrolysis, acidogenesis, acetogenesis and methanogenesis), a comprehensive understanding of the microbial behavior and population is an essential requirement for fundamental improvement of the anaerobic digestion process. Therefore, we recommend both qualitative and quantitative assessment of microbial community shifts during anaerobic digestion of slaughterhouse waste in batch reactors to study the transitional states involved during the process.

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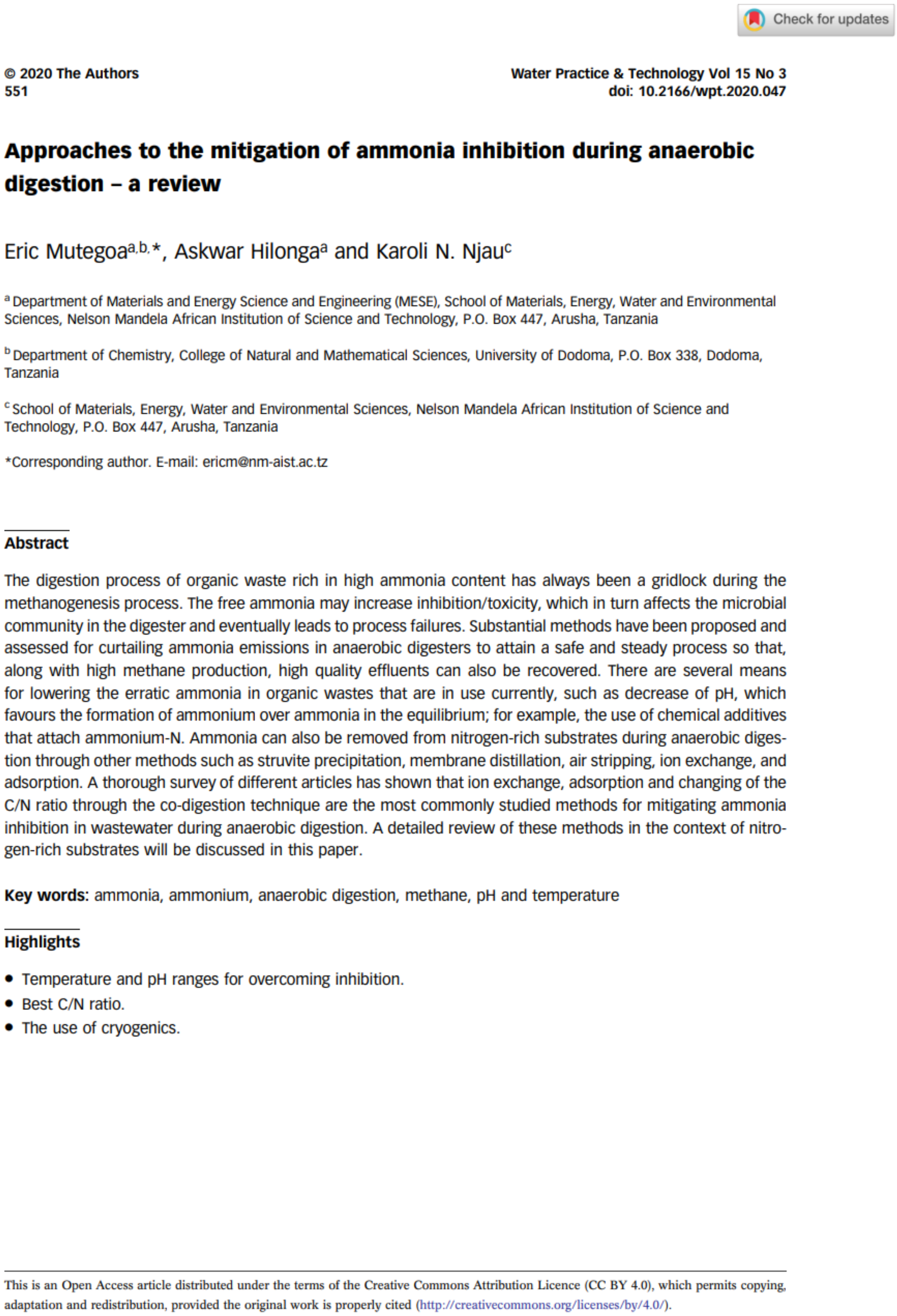
RESEARCH OUTPUTS

(i) **Publications**

(ii) **Poster Presentations**

Paper 1(Abstract)



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Approaches to the mitigation of ammonia inhibition during anaerobic digestion – a review

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Abstract

The digestion process of organic waste rich in high ammonia content has always been a gridlock during the methanogenesis process. The free ammonia may increase inhibition/toxicity, which in turn affects the microbial community in the digester and eventually leads to process failures. Substantial methods have been proposed and assessed for curtailing ammonia emissions in anaerobic digesters to attain a safe and steady process so that, along with high methane production, high quality effluents can also be recovered. There are several means for lowering the erratic ammonia in organic wastes that are in use currently, such as decrease of pH, which favours the formation of ammonium over ammonia in the equilibrium; for example, the use of chemical additives that attach ammonium-N. Ammonia can also be removed from nitrogen-rich substrates during anaerobic digestion through other methods such as struvite precipitation, membrane distillation, air stripping, ion exchange, and adsorption. A thorough survey of different articles has shown that ion exchange, adsorption and changing of the C/N ratio through the co-digestion technique are the most commonly studied methods for mitigating ammonia inhibition in wastewater during anaerobic digestion. A detailed review of these methods in the context of nitrogen-rich substrates will be discussed in this paper.

Key words: ammonia, ammonium, anaerobic digestion, methane, pH and temperature

Highlights

- Temperature and pH ranges for overcoming inhibition.
- Best C/N ratio.
- The use of cryogenics.

Paper 2(Abstract)

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Research article

Evaluating the level of ammonia and sulfide in the liquid phase during anaerobic digestion of slaughterhouse waste operating at mesophilic scale digester—the impact of inhibition and process performance

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Abstract: The performance of experimental batch-reactor loaded with slaughterhouse waste at mesophilic temperature was investigated as well as the inhibition of both ammonia and sulfide concentration in the aqueous phase. The digester was operated for 68 days by evaluating the process stability basing on controlling parameters such as pH, volatile fatty acids and alkalinity in relation to the methane produced. The maximum CH_4 content of 69.6% was achieved at 0.37

VFA/Alkalinity ratio and pH of 7.51 during day 37 of anaerobic digestion. However, a sudden increase of ammonia nitrogen in the digester from day 44 to day 68 decreased the methane content about 62.15% from 65% to 24.6%. Similarly, as the amount of sulfide content decreased in the liquid phase, gaseous H_2S was elevated up to 132 ppm in the 68th day. During this time, it was observed that the ratio of VFA/Alkalinity decreased to 0.16, with a very low concentration of VFA, which was 150.92 mg/L. This phenomenon indicated that all the acids produced were consumed by methanogens and ammonia inhibition was at the highest rate due to the increase of ammonia nitrogen concentration in the last days of digestion. Furthermore, among of peculiar characteristic shown by slaughterhouse waste is the ability to maintain the pH above 7 without the addition of any buffering agent throughout the AD process. Meanwhile, the evaluation of the level of both ammonia and sulfide in the aqueous phase revealed that the inhibitory effect of ammonia concentration was higher than sulfide concentration.

Keywords: ammonia; sulfide; methane; pH; VFA; alkalinity

Paper 3(Abstract)

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Effect of mixing ratios of natural inorganic additives in removing ammonia and sulfide in the liquid phase during anaerobic digestion of slaughterhouse waste

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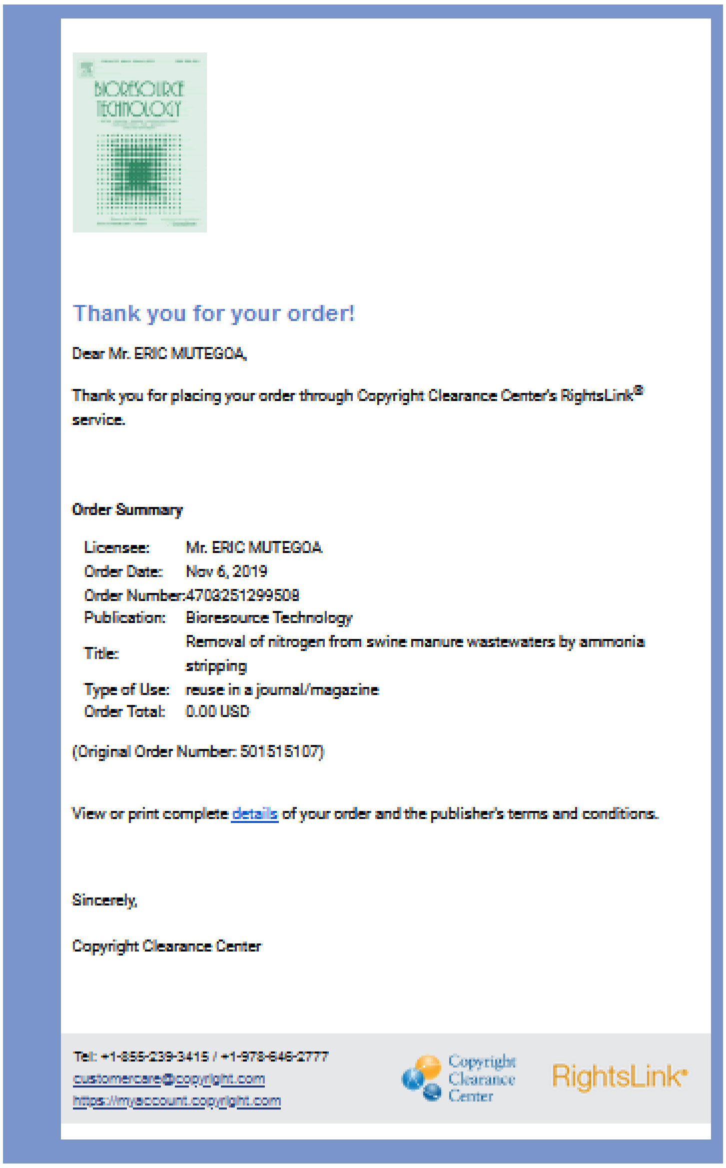
ABSTRACT

In this study, the efficacy of inorganic additives in the removal of total ammonia nitrogen (TAN) and sulfide in the aqueous phase of slaughterhouse waste undergoing anaerobic digestion in the batch reactor was investigated. A mixture of natural inorganic additives processed from the anthill and red rock soil samples collected from Arusha, Tanzania were used as adsorbents in different ratios. These materials were chosen in regard to their abundance in the local environment, surface properties, and elemental composition. Before analysis, the materials were pulverized and calcined at 700 and 900 °C for 2 h in a furnace and then sieved to 250 μm fine particle size. XRD analysis revealed that the anthill soil sample is endowed with major mineral phases of quartz and hematite while red rock soil contains albite, pyroxene, and quartz as predominant phases. The anthill and red rock soil samples calcined at 900 °C displayed higher BET surface areas of 815.35 and 852.35 m^2/g, respectively. The mixture of anthill soil and red rock soil in a ratio of 3:1 had a higher TAN removal efficiency of 92% at a contact time of 30 min compared to other ratios. On the other hand, a ratio of 1:2 showed a higher sulfide removal efficiency of 79% at a contact time of 60 min. Adsorption isotherm studies revealed that the Jovanovich model fitted better to the experimental data than the Langmuir and Freundlich models. The results demonstrated further that inorganic additives have a synergistic effect on stimulating methanogenesis as well as eliminating ammonia and sulfide during anaerobic digestion of slaughterhouse waste. Our findings demonstrate that anthill and red rock soils can be exploited as affordable, ecofriendly, and efficient adsorbents for mitigation of TAN and sulfide from the liquid phase and sustenance of methanogenesis.



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