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Cryptogamic packed biofilter as potential adsorbent for co2, h2s and nh3 impurities from biogas

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CRYPTOGAMIC PACKED BIOFILTER AS POTENTIAL ADSORBENT FOR CO_2, H_2S and NH_3 IMPURITIES FROM BIOGAS

Norbert Willibrord Temba

A Dissertation Submitted in Partial Fulfillment of the Requirements for the Degree of Master’s in Sustainable Energy Science and Engineering of the Nelson Mandela African Institution of Science and Technology

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ABSTRACT

The presence of elevated concentrations of carbon dioxide, hydrogen sulfide, ammonia and trace impurities in biogas affect its caloric value as well as causes corrosion and are extremely toxic. There are various methods for removal of these impurities, but most are chemically based, expensive and limited in use. In this work, cryptogams (moss) integrated with soil and biochar packed in a filter have been employed for simultaneous removal of CO_2, H_2S and NH_3, from biogas. Different soil types rich in metallic oxides at a different mass of (100 g, 150 g and 200 g) with a fixed mass of moss and biochar were tested in an on-site experiment to determine the removal efficiency (RE) and sorption capacity (SC). The adsorption dynamics of the filters were investigated at two flow rates, 80 ml/min and 100 ml/min, by determining removal efficiency. For the contribution of each substrate, sorption capacity and breakthrough time were determined by considering 5 g of each substrate that made up the filter. The soils with a high content of extractable cations showed excellent adsorption capacity for H_2S by about 20 g-S/100 g, which was higher than other adsorbents tested. It was found that integrated biofilter made up of bed arrangement of the soil, biochar and moss plant improved the quality of biogas with SC of 11 g-S and RE of 93% for H_2S, 72% for NH_3 and 68% for CO_2.

Keywords: Cryptogams, Biofiltration, Biochar, Removal efficiency, Sorption Capacity.

DECLARATION

I, NORBERT W. TEMBA, 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 concurrently submitted for a degree or similar award in any other institution.

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Name and signature of candidate **Date**

The above declaration is confirmed

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Name and signature of supervisor 1 **Date**

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Name and signature of supervisor 2 **Date**

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CERTIFICATION

The undersigned certify that they have read and hereby recommend for acceptance by the Nelson Mandela African Institution of Science and Technology a the dissertation entitled: ‘‘Cryptogamic packed biofilter as potential adsorbent for CO_2, H_2S and NH_3 and impurities from biogas’’ and recommend for examination in partial fulfillment of the requirements for the degree of Masters in Sustainable Energy Science and Engineering of The Nelson Mandela African Institution of Science and Technology.

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DEDICATION

This work is dedicated to my family, friends and my co-workers who have always been there supporting me throughout every step of the way.

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LIST OF ABBREVIATIONS AND SYMBOLS

AD	Anaerobic Digestion
VOC	Volatile Organic Compounds/gases
RE	Removal Efficiency
SC	Sorption Capacity
BT	Breakthrough Time
C_i	Initial Concentration
C_f	Final Concentration
CDM	Clean Development Mechanism arrangement
UN	United Nations
REDDs	Reducing Emissions from Deforestation and Degradation
RB	Rhodamine B
AC	Activated Carbon
CHP	Combined Heat and Power Engines
APC	Air Pollution Control
SOC	Soil Organic Carbon
VSA	Vacuum Swing Adsorption
CEC	Cation Exchange Capacity
Raw gas	Untreated Biogas

CHAPTER ONE

INTRODUCTION

1.1 Background of the Problem

The increase in energy demands due to population growth, depletion of worldwide oil reserves and the problem of harmful emissions emanating from fossil fuel have put pressure on the world's countries to use renewable energy. One of the renewable energy sources is biogas. It provides the more reliable option of a sustainable form of energy as it is derived from energy crops, agricultural wastes, agro-industrial wastes, municipal waste, etc (Longdong *et al.*, 2014). Biogas production from anaerobic digestion of lignocellulosic biomass in the form of wood residues and agricultural wastes has been attracting wide attention due to their accessibility and environmental sustainability of these materials (Mulat *et al.*, 2018). The gas is mainly composed of methane (CH_4) and carbon dioxide (CO_2) with smaller amounts of hydrogen (H_2S), ammonia (NH_3). In most cases trace amounts of hydrogen sulfide (H_2), saturated or halogenated carbohydrates, nitrogen (N_2) and oxygen (O_2) can be found in the biogas (Persson *et al.*, 2006). Typical raw biogas consists of about 55–65% methane, 30–45% carbon dioxide, traces of hydrogen sulfide, fractions of water vapors and other contaminant gases (Kapdi *et al.*, 2005). Biogas has the potential to counteract many health and environmental impacts connected with other forms of traditional biomass energy. Apart from supplying energy and fertilizer, biogas can also be used as an alternative for the mitigation of greenhouse gas emissions and reduction of global warming.

Biogas produced from digesters is used mainly for cooking and rarely for heating, lighting and electricity generation, simply because of the presence of hydrogen sulfide and other impurities, which together leads to corrosion of metal components in engines and gas burners (Abatzoglou *et al.*, 2009). For biogas to be utilized effectively, purification is required to improve its efficiency and caloric value. Current technologies to purify biogas by removing H_2S, CO_2 and NH_3 use chemical liquids, membrane separation, biological filters, or activated carbon, which are not only costly and cumbersome to use but also result in low removal efficiencies (Ryckebosch *et al.*, 2011).

According to the Kyoto protocol on emissions reduction projects for developing countries, biogas is singled out as a potential renewable energy replacement for kerosene in rural areas in the Clean Development Mechanism arrangement (CDM). Further emphasis by the United

Nations (UN) program of Reducing Emissions from Deforestation and Degradation (REDDs), acts as a recommended initiative for developing countries to reduce emissions and invest in low carbon alternatives such as biogas (Smith *et al.*, 2011).

Soil is the topmost layer of the earth's surface which supports life and primarily made up of a mixture of plants and organic remains, as a result of in situ weathering of rock materials or the accumulation of mineral matter transported by water, wind, or ice. It acts as media for plant growth comprised of organic and inorganic materials by providing physical support, water and nutrients (Nortcliff *et al.*, 2000). Soil differs by its composition and structure. The presence of microbial activities as part of the soil has been studied to account for its usefulness and consider some of the future potential and limitations of its use as a method of air purification for both environmental applications and in the context of bio regenerative life support systems (Nelson *et al.*, 2011). The use of biofilters can improve indoor air pollution, outdoor air emissions of toxic gases thus aiding to reduce the global warming impact of methane (biogas). Also the presence of iron oxide (Fe_2O_3) rich material is a simple, efficient method to remove H_2S in biogas since iron oxide readily reacts with H_2S to form iron sulfide (Fe_2S_3) when biogas passes through it (Zicari, 2003).

Soils rich in metallic oxides are found to be effective in the removal of H_2S (Abatzoglou *et al.*, 2009). A process of soil biofiltration is based on the using of a bed of materials set up such that perforated pipes can deliver the discharge air as it passes through a series of moist, aerated biological material where the gas is absorbed and dissolved in soil solution (Nelson *et al.*, 2011). Soil biofiltration is considered among the best available technology and more fool-proof operation, because of lower investment and operating costs; they are suitable where the pollutant loading is in low concentration or low volume discharge (Leson *et al.*, 1991). Primarily, they have been used for the control of foul odors and reduction in potentially toxic trace gases. The design employs either soil medium or compost in a system that makes use of natural soil processes for dissolution, adsorption and microbial metabolism of inorganic gases and volatile organics present in the effluent air (Nelson *et al.*, 2011).

Another component that has been investigated for air biofiltration is biochar. It can be defined as a black carbon-rich material made up from the decomposition of plant-derived organic matter (waste biomass) in a low or zero oxygen environmental (i.e. pyrolysis or gasification) to release abundant energy gases which are used for power generation or production of liquid fuels (Ahmad *et al.*, 2014; Manyà, 2012). In another more descriptive definition biochar is the carbonaceous solid product made from the thermochemical conversion of organic material in an oxygen-depleted environment (Shackley *et al.*, 2012). Biochar research has shown considerable key findings in carbon sequestration, agronomics, greenhouse gas emissions, soil quality, soil acidity, soil salinity and soil fertility (Lehmann *et al.*, 2003; Van Zwieten *et al.*, 2010).

Furthermore, studies by Agegnehu *et al.* (2016) and Schulz *et al.* (2013) showed improvements in soil physicochemical properties including soil organic carbon (SOC) and cation exchange capacity (CEC) by using co-composited biochar as well as biochar-composite mixes in soil modifications.

Figure 1: Cryptogamic cover in different environment

Furthermore, it is known to be an efficient and cost-effective sorbent for different kinds of pollutant removal. Biochar contains unmodified activated carbon which mechanically removes sulfur from active sites by deposition in the presence of water which slows down the degeneration process (Primavera *et al.*, 1998). For example, straw-based biochar was identified as a cost-effective substitute for activated carbon for its adsorptive ability towards dye removal in wastewater (Qiu *et al.*, 2009). The results showed biochar was slightly more effective than AC to adsorb RB (rhodamine B) due to the RB–Biochar electrostatic interactions and RB protonation at low pH.

Cryptogamic covers are photoautotrophic communities, consisting of cyanobacteria, algae, fungi, lichens and bryophytes, that is, liverworts and mosses in variable proportions (Lenhart *et al.*, 2015). These communities can provide food webs by photosynthesis and nitrogen fixation, which is particularly important in arid regions and other terrestrial environments with a low abundance of organic nutrients. Cryptogams are estimated to be responsible for almost half of the total terrestrial biological nitrogen fixation of $\approx 49 \cdot 10^9$ kg $year^{-1}$ and carbon uptake of $\approx 3.9 \cdot 10^9$ ton $year^{-1}$ which amounts to $\approx 7\%$ of the net primary production of terrestrial vegetation (Elbert *et al.*, 2012). Example of cryptogams are as shown in Fig. 1.

Lichens and mosses are cryptogamic organisms that exist in almost all terrestrial ecosystems and by virtue of their ability to tolerate long periods of drought may even colonize areas with extreme environmental conditions. Because of their high surface: volume ratio, the simple anatomy and absence of a cuticle they accumulate heavy metals and concentrating them in their tissues (Adamo *et al.*, 2003). These organisms are also considered to be effective in recording relative spatial and temporal deposition patterns of contaminants due to their characteristics in accumulating and retaining a variety of contaminants. Integrating plants and soil biofiltration for the elimination of technogenic and volatile organic gases (VOC) has been studied to provide means of biological purification without the use of consumables (Nelson *et al.*, 1994; Wolverton *et al.*, 1984). Incorporating different media in packed bed filter has shown successful results in biofiltration for a wide range of air pollutants and VOCs (Dumont, 2015; Nelson *et al.*, 2011; Yoon *et al.*, 2002). Natural organic medium primarily composed of compost, peat, leaves, wood bark and soil has been studied for the removal of toluene contaminated air and VOCs (Sorial *et al.*, 1997; Yoon *et al.*, 2002). This study aimed to apply the properties of cryptogams integrated with soil and biochar packed in a filter to simultaneously remove CO_2, H_2S and NH_3 from biogas.

1.2 Statement of the Problem

Significant biogas yields have already been achieved from the various feedstocks; however, the quality of the gas produced has been a great challenge. The presence of CO_2 and H_2S significantly reduces the fuel value and performance of biogas in both domestic and industrial applications. Therefore, proposing inexpensive and environmentally friendly methods of purification by eliminating unwanted gases, for example, CO_2, H_2S and NH_3, could enable easy compression for transportation, reduce toxic emissions and finally add value to the biogas. Carbon dioxide present in the biogas composition accounts for increased corrosiveness of engines and storage facilities, toxicity in animals and plants and lowers efficiency and calorific value of the fuel. The combustion of H_2S results in the release of sulfur dioxide (SO_x), which is a greenhouse gas. The H_2S is an inorganic acid that attacks the surface of metals when they are placed in direct contact (Gosh, 2007). Furthermore, NH_3 insignificant concentrations cause complications for gas engines and during combustion emitted gases (NO_x) are often limited by manufacturers. Studies show that combustion of ammonia leads to the formation of nitrous oxide (NO_x) which is very poisonous to both plants and animals (Persson *et al.*, 2006).

The present technology used in biogas purification includes; membranes, chemical and biological scrubbing which are very expensive require substantial energy inputs and produce chemically harmful byproducts. Also, the chemicals used are corrosive and hence require safety precautions both in design and operations. This study aims at using the properties of moss integrated with iron-rich soil to provide an inexpensive and effective filter that uses minimum energy to operate.

1.3 Rationale of the Study

All gases produced from the biodigester, only methane is combustible, carbon dioxide, hydrogen sulfide and ammonia reduce the fuel efficiency of the biogas and therefore need to be removed or significantly reduced to the very minimum. By purifying the produced biogas, it will enable the fulfillment of needed requirements and standardization for gas appliances, easy transportation to various locations and as a result, leads to increase heating value for domestic and industrial applications.

1.4 Objectives

1.4.1 General Objective

To fabricate a prototype of a cryptogamic integrated biofilter for the adsorption of carbon dioxide, hydrogen sulfide and ammonia from biogas.

1.4.2 Specific Objectives

(i) To analyze soil composition and physicochemical properties.
(ii) To determine effective moss-soil optimal composition for biofiltration process.
(iii) To assess the effect of varying experimental parameters on the performance efficiency of biofilter.

1.5 Research Questions

(i) What is the soil organic matter and iron oxide composition of soil samples?

(ii) What is optimal moss- soil filters for effective removal of CO_2, H_2S and NH_3 from biogas?

(iii) What are the optimum experimental conditions of the filters for active biogas purification?

1.6 Significance of the Study

According to the fact that of all gases produced from the biodigester, only methane is combustible, carbon dioxide and hydrogen sulfide reduce the fuel calorific value hence its efficiency. Removal of these impurities from biogas will improve its usage and in turn reducing environmental pollution.

1.7 Delineation of the Study

The study was conducted experimentally on a domestic biogas digester. The biofilter was fabricated at the Laboratory using the components (substrates) involving soil, biochar and cryptogams (moss) in variable proportion, to investigate its performance in biogas purification. The parameters that were varied include mass, soil type and flow rate. The results were used to extrapolate the removal efficiency and sorption capacity of each component to determine its practicability and sustainability.

CHAPTER TWO

LITERATURE REVIEW

2.1 Biogas Composition

The main composition of biogas typically ranges 50 to 65% CH_4, 30 to 45% CO_2, traces of H_2S, NH_3 and moisture. For example, in literature, it is reported the CH_4 is the main component of biogas in a range between 40 and 70% and lower heating value between 15 to 30 MJ/Nm^3 (Tippayawong *et al.*, 2010). The exact composition depends on the type of feedstock used and anaerobic conditions. Table 1 presents typical biogas composition, which depends on the feedstock used. Feedstock refers to any substrate that can be converted to methane by anaerobic bacteria (Steffen *et al.*, 1998).

Table 1: Composition of biogas, depending on the feedstock

Gas	Units	Organic Waste	Sewage	Landfill
Methane	$\%_{vol}$	60 – 70	55 – 65	45 – 55
Carbon dioxide	$\%_{vol}$	30 – 40	35 – 45	30 – 40
Nitrogen	$\%_{vol}$	<1	<1	5 – 15
Hydrogen Sulfide	ppm_v	10 – 2000	10 – 40	50 – 300

Rasi *et al.* (2007)

The biogas produced from organic waste on a farm varies depending on the feed stream. Biogas produced from the cow slurry contains 55-75% CH_4, 70-80% CH_4 from pig slurry, 60-80% CH_4 from chicken slurry and 70-80% CH_4 from food slurry (Steffen *et al.*, 1998). As observed organic wastes produce the high H_2S content. Biogas also contains other compounds in trace amounts such as halogenated compounds, siloxanes and aromatic compounds. Water vapor is also present in biogas as a product of anaerobic digestion process and may also contain some dust particles (Petersson *et al.*, 2009).

Untreated or raw biogas is normally saturated with water and absolute water quantity depends on the temperature of the biodigester. It has been studied by Ryckebosch *et al.* (2011), that at 35°C the water content is approximately 5%. However, it should be removed before use for most energy applications. The levels of H_2S has been reported to in some cases to be in a range of 0-0.4%v/v of total biogas (Kuria *et al.*, 2008). This gas is corrosive on metallic appliances such as copper, steel, iron and lead pipes and gas holders if not removed from the biogas (Horikawa *et al.*, 2004). The concentration of H_2S above this level should be removed from the biogas before use as reported by Tippayawong *et al.* (2010). When biogas is burned SO_2/SO_3 is emitted which is even more dangerous and poisonous than H_2S itself. During combustion NH_3 and halogenated hydrocarbons produce harmful and corrosive products, which can immensely damage engines and pipelines (Persson *et al.*, 2006). Upgrading biogas to natural gas quality is also a critical multi-step procedure. After removal of water (vapor), H_2S, trace compounds of siloxanes and NH_3, the removal of CO_2 is essential to obtain the quantity that meets the Wobbe index. According to Hagen *et al.* (2001) the Wobbe index is an indicator of the quality of a fuel gas, measured from heat produced by burning through a defined orifice under standard temperature and pressure conditions. If the Wobbe index of the natural gas is higher than the minimum limit, the mixture of natural gas and upgraded gas can meet the pipeline specification for the national gas grid. Upgrading biogas by removing CO_2, lowers the relative density and increases the calorific value and thus increasing the Wobbe index, as shown in Fig. 2.

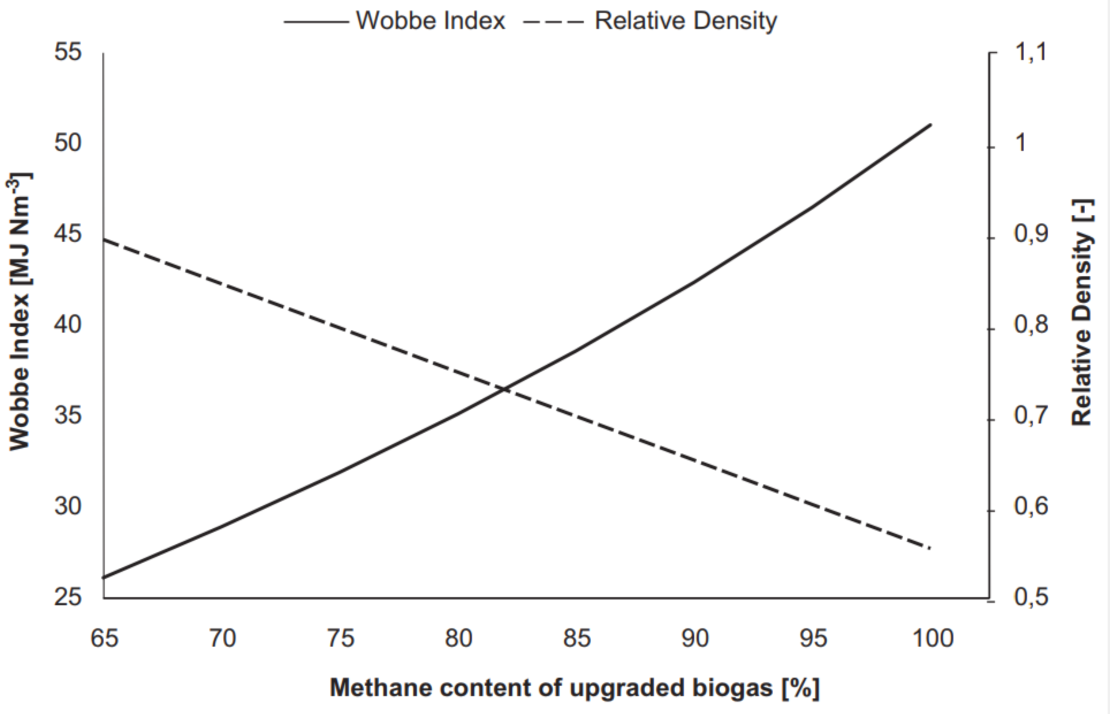

Figure 2: Wobbe index and relative density as a function of CH_4 content (Hagen *et al.*, 2001)

Carbon dioxide removal at an industrial scale is nowadays achieved by physical/chemical technologies based on their high degree of success and commercial availability. These removal methods a) Pressure Swing Adsorption, b) Vacuum Swing Adsorption (VSA), c) Membrane separation, d) Cryogenic separation and e) Biological removal.

2.2 Gas Utilization

As a renewable fuel, biogas can be used for various applications designed for natural gas. However, not all gas appliances require the same gas standards. There is a significant difference between daily requirements for stationary biogas applications and fuel gas or pipeline quality. Boilers, Gas engines, diesel engines and all other combined heat and power engines (CHP engines) have different standards for gas quality to be used. As shown in Table 2, unwanted gaseous components need to be removed depending on the biogas utilization.

Table 2: Requirement to remove gaseous components depending on the biogas utilization (Petersson *et al.*, 2009)

Application	H_2S	CO_2	H_2O
Gas heater (boiler)	< 1000 ppm	no	no
Kitchen stove	yes	no	no
Stationary engine (CHP)	< 1000 ppm	no	no condensation
Vehicle fuel	yes	recommended	yes
Natural gas grid	yes	yes	yes

In fuel application for vehicles, raw biogas cannot be used as it affects engine performance; SO_2 and SO_3 formed during the combustion of H_2S, which are more toxic and causes corrosion as a result it brings about maintenance concerns. Besides, NH_3 causes the formation of NOx, when dissolved in water becomes corrosive and leads to an increase in antiknock properties of engines. By upgrading the gas, it aids to the following advantage a) high calorific value, b) constant gas quality, c) less corrosion caused by high levels of H_2S and NH_3, d) less clogging due to high water content. The upgraded biogas is called biomethane, a product equivalent to natural gas with 96 – 98.5% methane (Bauer *et al.*, 2013). The calorific value of biogas is between 20 – 28 MJ/m^3 depending on the CH_4 content meanwhile that of liquefies pressurize gas LPG is 36 MJ/m^3 (Salum *et al.*, 2009).

Quality of biomethane is an important criterion for a particular application for example (transnational) to be fed into the gas grid and the end-use applications. Compared to conventional fuels, the level of standardization is sparse for gaseous fuels. The international

ISO (International Organization for standardization) issued a natural gas standard, ISO 13686:1998 "Natural gas - Quality designation" and a standard for compressed natural gas, ISO 15403 Natural gas – Natural gas for use as a compressed fuel for vehicles (Thrän *et al.*, 2014). This standard is essential based on its application specifically for natural gas grids and vehicle fuel as shown in Table 2. According to Krich *et al.* (2005) there are about three steps to upgrading biogas to biomethane, which are; removal of H_2S, removal of moisture and removal of CO_2. Some of the methods used for H_2S removal involve:

(i) Air injected into the biodigester

(ii) Reaction with iron oxide or hydroxide (iron sponge)

(iii) Use of activated-carbon sieve

(iv) Water scrubbing

(v) Biological removal on a filter bed / Biological desulphurization

According to Pokorna *et al.* (2015) biological desulphurization is the addition of air into the storage tank which at the same time serving as the gasholder. It is one of the simplest methods of H_2S removal in the digester as microorganisms (sulfur-oxidizing bacteria) reduce the H_2S concentration by 95% to less than 50 ppm. Elemental sulfur is produced from the oxidation of Hydrogen sulfide, while phototrophic sulfur-oxidizing bacteria reduce CO_2 and incorporates it into organic compounds. The process is considered as chemosynthesis since the bacteria do not release oxygen to the atmosphere as shown in Eq. (2.1) below:

$$2\,H_2S + CO_2 + \text{light} \rightarrow 2\,S^0 + CH_2O + H_2O \quad \ldots\ldots (2.1)$$

Some other industrial methods that have been applied to eliminate CO_2 and H_2S from raw biogas are:

(i) Pressure swing adsorption

(ii) Water scrubbing

(iii) Chemical scrubbing with amines

(iv) Membrane separation

(v) Cryogenic separation

In addition to H_2S and CO_2, removal of trace impurities notably phosphorus compounds, allows biogas to be used in the production of hydrogen for fuel cells (Cebula, 2009). Chemical absorption of CO_2 and H_2S by aqueous solutions in a packed column was also investigated by (Tippayawong *et al.*, 2010). The aqueous solutions employed were sodium hydroxide, calcium hydroxide and mono-ethanolamine. The results revealed that over 90% removal efficiency by aqueous solution with CO_2 and H_2S was removed below the detection limit, thus creating CH_4 enriched fuel. Therefore, removal of multiple impurities in the biogas is useful in raising its high value.

2.3 Working Principle of Air Biofilter

Biofiltration refers to the process air pollution control (APC) technology in which off-gases containing biodegradable volatile organic compounds (VOC) or inorganic air toxins are vented through a biologically active material (Leson *et al.*, 1991). This process employs biomonitors, bio accumulators and bioindicators in filtering air impurities using naturally occurring plants (Mosses, Lichens and Liverworts) and inorganic materials. Application of lichens and mosses as biomonitors of air pollution has been studied since these organisms rely on atmospheric sources for nutrients and in addition to that, they do not shed plant parts as readily as vascular plants. Among the characteristic features of these organisms is to accumulate and retain a range of contaminants. As a result, they are very useful in recording relative spatial and temporal deposition patterns of contaminants (Nash III *et al.*, 1988).

In a survey to assess the contribution of thermal springs and fumaroles to environmental levels of selected trace elements employing lichens and mosses to be used as bio accumulators suggested that lichens and mosses can be preferred as accumulators of As, Cd, Cu, Mo and S deposition. Concentration differences between lichens and mosses were statistically significant for Al, B, Fe, Hg, Pb, Sb and Zn, with mosses retaining higher values than lichens except for Hg and Zn (Loppi *et al.*, 2000). They have also shown high tolerance of ammonia uptake and nitrogen fixation up to the annual average of 0.001 mgm^{-3}, which is the critical level for annual average NH_3 concentrations for sensitive ecosystems (i.e. those in which lichens and bryophytes are important components) (Cape *et al.*, 2009).

Removal of NH_3 is essential to increase the calorific value of biogas. In most cases, NH_3 is mostly formed during degradation of proteins and its concentration depends upon the substrate composition and the pH in the digester. To separate ammonia from the mixture of other impurities the gas has to be dried and upgraded, therefore a separate cleaning step is in most cases not necessary (Petersson *et al.*, 2009). Alternatively, NH_3 can also be removed from the gas by a washing process with diluted nitric or sulfuric acid. But the use of these acids demands stainless steel installation which can be expensive for small scale applications like biogas cleaning (Ryckebosch *et al.*, 2011). In addition to that, Chung *et al.* (2000) experimented on biotreatment of H_2S and NH_3 containing waste gases by co-immobilized cells biofilter. The biofilter was packed with co-immobilized cells, H_2S and NH_3 gas mixture were continuously supplied at various ratios. The results revealed that the removal efficiency remained above 95% with disregard of the ration of H_2S and NH_3 used.

2.4 Introduction to Cryptogams

The Plants are autotrophic organisms as they can synthesize their food with the help of sunlight and photosynthetic pigments from carbon dioxide and water. They exist in both aquatic and terrestrial habitats. They are of different shapes and sizes. Some plants are microscopic and some grow up to 100 m. Plants are essential in regulating biogeochemical cycles and also in the exchange of gases that support life in our biosphere. Plants can be categorized into two groups namely; cryptogams and phanerogams (Saini, 2010). Cryptogams are made up of flowerless or seedless plants while phanerogams are flowering or seed-bearing plants. Cryptogams are made up of bryophytes, lichens, fungi and algae. Mosses are grouped in bryophytes. Bryophytes tend to diverge from vascular plants especially in influencing cycles of elements, energy and water as a result of their unique physiology and ecology. For example, they can sustain longer periods of water scarcity than vascular plants and can recover quickly with hydration. As a result of a poorly developed conduction system, water and solutes are taken up over the entire plant surface.

The absence of both gametophyte stomata and effective cuticles allows a free exchange of solutions and gases across its cell surface (Turetsky, 2003). The property makes bryophytes effective in trapping water and nutrients. Furthermore, it subjects them to more sensitivity to atmospheric depositions over vascular plants. It has been observed that moss accumulates traces of SO_2 more expeditiously than the leaves of vascular plants (Winner, 1988). Mosses and lichens have been experimented as air pollutant monitors and also biomonitors of trace metals (Adamo *et al.*, 2003). The observations of this by Bargagli *et al.* (2002) and Adamo *et al.* (2003) are as shown in Table 3.

Furthermore, there have been studied to improve the carbon net uptake and nitrogen fixation in different types of ecosystems on a continental and global scale (Elbert *et al.*, 2012). Further studies aimed at analyzing the effectiveness of lichens and mosses in geothermal power plants as biomonitors of trace elements, the result showed both organisms could be used as biomonitors of elements arising from geothermal emissions. However, Bargagli *et al.* (2002) observed that they can’t be used conversely in mineral deposits as biomonitors of metals and metallic compounds. In urban areas, where mosses and lichens are scarce, the bags technique has been developed to monitor air pollution.

Table 3: Trace element concentration (µg g^{-1}) in mosses and lichens studied from relatively unpolluted areas in Italy (Adamo *et al.*, 2003)

Element	**Mosses**			**Epiphytic lichens**		
	Sphagnum capilifolium	**Hylocomium splendens”**	**Hypnum cupressiforme”**	**Pseudevernia furfuracea**	**Foliose (e.g. Parmelia,Hypogymnia”**	**Fruticose (e.g Ramalina, Evernia)**
A1	118	700	1600	415	n.d	120-150
As	0.11	n.d	n.d	0.15	0.7-2.0	0.3-1.5
Cd	0.38	0.3	0.3	0.46	<0.1-0.3	<0.1-0.2
Co	0.43	n.d	n.d	0.23	<0.1-0.3	<0.1-0.2
Cr	1.60	0.9	2.4	2.23	1-4	<1-3
Cu	5.54	8.6	8.4	5.42	4-10	4-10
Fe	675	457	1290	363	150-300	150-300
Mn	552	150	178	29.9	20-80	20-60
Mo	0.41	n.d	n.d	0.26	<0.1-0.5	<0.1-0.5
Ni	2.35	1.3	1.8	1.81	1-3	<1-2
Pb	18.87	17.0	15	23.0	1-8	1-5
Ti	11.46	n.d	n.d	8.73	5-35	5-20
V	1.55	n.d	n.d	1.49	<1-3	<1-2
Zn	83	32.0	26	99	20-90	20-70

2.5 The Efficiency of Cryptogams and Soil Biofilter in Biogas Purification

Bacteria and fungi have been widely considered in the treatment of a range of environmental pollutants, as degradants which involves the breakdown of organic compounds by either through biotransformation into less complex metabolites or through mineralization to form inorganic minerals, H_2O, O_2 (aerobic) or CH_4 (anaerobic). Fungi have also been investigated concerning their capacity to remove volatile contaminants in air biofilters. The use of fungi and other microorganisms in biofiltration have reached a relatively high elimination capacity and are resistant to low pH values and moisture content (Kennes *et al.*, 2004). In this case, polluted air flows through a porous matrix that acts as a support for microorganism development. By controlling the humidity of the medium fungi can be enriched over bacteria.

Further studies have also concluded that various species of cryptogams can be used to sight metal deposition of the surrounding the ecosystem quite quickly and at a lower cost. The absence of a well-developed cuticle and roots in mosses and lichens, causes these organisms to rely mainly on atmospheric deposits for nourishment. Also, these organisms do not shed plant parts and they accumulate atmospheric pollutants at higher concentrations than that of vascular plants (Bargagli, 1989; Bargagli *et al.*, 2002; Groet, 1976; Rühling, 1994). Some of the species cryptogams in the form of moss Hypnum cupressiforme and the epiphytic lichen Parmelia caperata were found to be effective biomonitors of trace metals in the atmosphere (Bargagli *et al.*, 2002). Therefore, these species effectively use fine particles as a means to ensure their survival. As its true nature, under a controlled environment, they can absorb a significant amount of pollutants. This gives room for further research in integrating them with other bio accumulators so they can coexist to perform this particular function. Soil and sand have also shown significant capacity in adsorbing trace elements and gas from the atmosphere. Studies also observed that brown soil in the form of allophonic soil contains iron in the form of hydrated iron (Fe_2O_3) (Dillon, 1990). The iron oxide in these soils would readily react with hydrogen sulfide (H_2S) to form iron sulfide (Fe_2S_3) and water (H_2O) when the gas mixtures passed through the soil filter.

$Fe_2O_{3(s)} + 3H_2S_{(g)} \rightarrow Fe_2S_{3(s)} + 3H_2O_{(l)}$ ………………………………………………………. (2.2)

$2Fe_2S_{3(s)} + 3O_{2(g)} \rightarrow 2Fe_2O_{3(s)} + 6S_{(s)}$ …………………………………………………… ……. (2.3)

Since elemental sulfur is thought to build upon the surface of sulfide minerals during their oxidation by O_2 as shown in Eqn. 2.3, the ability of acidophilic bacteria to oxidize elemental sulfur using ferric iron as an oxidant is geochemically in the leaching of sulfide ores to form sulphates (Sato, 1960).

$S + 6Fe^{3+} + 4H_2O = HSO_4^- + 6Fe^{2+} + 7H^+$ ………………………………………………... (2.4)

$2S° + 3O_2 + 2H_2O = 2HSO_4^- + 2H^+$ ……………………………………………..……... (2.5)

Eqn. 2.4 (assuming pH 2) is -75 kcal and the free energy of the reaction Eqn 2.5 (assuming pH 2) is -124 kcalS^{-1} atom (-247 kcal for the whole reaction), there is more energy available using O_2 than Fe^{3+} as electron acceptor (Brock *et al.*, 1976).

Soil supports the growth of bioindicators (Mosses and Lichens) which filters particulate matter and mineral elements from the atmosphere. The primary source of carbon for moss and lichens is mainly CO2. The use of soil bio-filtration provides a cheap solution in terms of investment capital and operating energy costs to handle contaminants in moderate concentrations. The soil biofilter can be designed to improve performance and optimize efficiency through handling temperature, pH, moisture content, airflow rates and soil organic matter (Nelson *et al.*, 2011).

2.6 Absorption of Sulfides by Oxides

Many industrial by-products specifically from oil refineries contain H_2S present from coal gas. Broekhuis *et al.* (1992) presented a medium-temperature process for H_2S removal using aqueous metal sulfate solutions. The results were the metal sulfide would oxidize with ferric ion to form sulfur as shown in Eqn. 2.3. Rodriguez *et al.* (1998) investigated the reaction of H_2S and S_2 with metal/oxides surface in relation to band-gap size and chemical reactivity. The theoretical method used was ab initio self-consistent field (SCF) calculations and a simple model that combines perturbation theory with Huˆckel and tight-binding methods on a series of oxides (Al_2O_3, Cr_2O_3, Cr_3O_4, Cu_2O, ZnO) and metal/oxide (Cu/ Al_2O_3, Cu/ZnO) surfaces.

The results showed that for the adsorption of S2 on Al_2O_3, Cu_2O and ZnO, the surface chemistry of the molecules on oxides that have a relatively small band-gap is much higher than on alumina. Therefore, the metal and metal oxides of ZnO and Cu_2O are more reactive towards sulfur than sites of alumina (Al_2O_3) as shown in Fig. 2.

Also, wood chips impregnated with iron oxide have been experimented to selectively adsorb H_2S and mercaptans. The reaction of Iron oxides and sulfur leads to the formation of insoluble iron sulfides. Additionally, it’s possible to prolong the bed life by admitting air, which leads to the formation of elemental sulfur and regenerating the iron oxide. The media will need to be replaced once it becomes clogged with elemental sulfur.

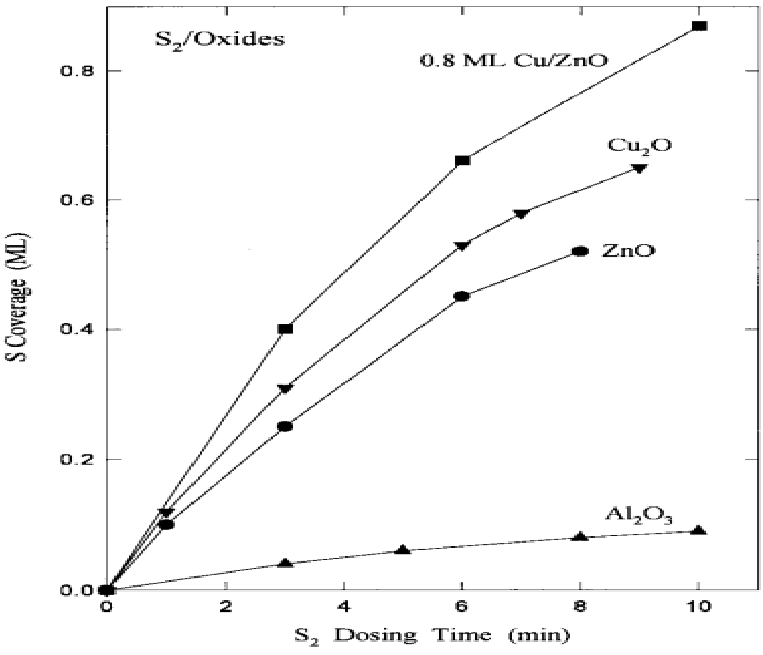

Figure 3: Amount of sulfur adsorbed after dosing S_2 to Al_2O_3, ZnO, Cu_2O and $Cu_{0.8}$/ZnO at ~300 K (Rodriguez *et al.*, 1998)

$MeS_{(s)} + 2Fe^{3+} \rightarrow Me^{2+} + 2Fe^{2+} + S$ …………………………………………….. (2.6)

$H_2S + ½\, O_2 \rightarrow S + H_2O$ ………………………………………………………… (2.7)

This happens as the sulfur stays on the surface of the oxide allowing the process to be repeated for a specific period until the interstices between the oxide's particles are full. Due to S^0 build-up and water hydration loss, ferric iron (iron sponge) activity is reduced to about one-third per each regeneration cycle (Kohl *et al.*, 1997). The removal efficiency of this technique depends mostly on the temperature, moisture content and pH of the material used during the purification process. The use of ferric oxide is advantageous as it is cheap and the easiness of operation and maintenance. While the disadvantage is the amount of heat released during the regeneration process.

2.7 Absorption of CO_2 and H_2S by Biochar

Biochar can be defined as a carbon-rich product formed from thermal decomposition of organic material under a limited supply of oxygen (O_2) and at relatively low temperatures < 700°C (Hale *et al.*, 2011). Normally recognized as a multifunctional material, biochar has been explored for agricultural and environmental applications. Biochar is also known to act as a super sorbent for organic contaminants in soil/ sediment. The use of biochar has also been recommended for various horticultural contexts. It acts as a sponge in the soil, absorbing and retaining water, gases and solutions. Adding biochar to the soil helps in promoting the growth of vegetation by improving soil chemical properties which includes nutrient retention and nutrient availability. It also improves hydrophysical soil characteristics (bulk density, soil permeability, field capacity) and biological properties (Surda *et al.*, 2016). Biochar research has considerably progressed with significant key findings particularly on agronomic benefits, carbon sequestration, greenhouse emissions, soil quality, soil fertility, soil acidity, soil salinity, etc.

Lehmann *et al.* (2015) with further research into biochar- compost mixes and co- composted biochar as soil amendments. Another important fact about biochar is its resistance to attack and decomposition by microorganism, the main reason being its carbon atoms are firmly bound to one another. Other studies to investigate the removal of H_2S and CO_2 from biochar and other carbon-rich substrates have been conducted. Lin *et al.* (2001) experimented on the removal of H_2S from coal bottom ash. The results showed each gram of coal ash could remove up to 10.5 mg of H_2S. In another study Sethupathi *et al.* (2017), tested biochar as a potential adsorbent to CH_4, CO_2 and H_2S gases. This was done by studying the breakthrough times of H_2S, CO_2 and CH_4 for different biochar obtained from oak, perilla and soybean and the simultaneous removal of multiple gases.

The results concluded that CH_4 was not well adsorbed by the subjected biochar whereas CO_2 and H_2S were successfully captured. Table 4 as described by Sethupathi *et al.* (2017) shows the adsorption capacity of biochar during the experiment. Thus, it has the potential to be used as a substrate for the biogas purification process. Juárez *et al.* (2018) investigated the possibility of purifying biogas from a small-scale biogas plant by entrapping CO_2 and H_2S using biomass ash. The results showed that CO_2 was trapped for a few hours while it took H_2S up to 34 days with H_2S absorption in the range of 0.56 - 1.25 kg ton^{-1} of ash.

Table 4: Adsorption capacity of biochar during simultaneous and single-gas presentation (Sethupathi *et al.*, 2017)

Biochar	Simultaneous			Single		
				H_2S	CO_2	CH_4
Perilla	0.208	0.126	0.000	0.537	2.312	0.099
Korean oak	0.022	0.027	0.000	0.178	0.597	0.092
Japanese oak	0.018	0.012	0.000	0.167	0.379	0.064
Soybean stover	0.072	0.082	0.000	0.308	0.707	0.094

2.8 Performance Analysis of Other Purification Methods

Chemical, biological and physical methods have been employed for biogas purification. These methods as studied by Iovane *et al.* (2014), Ryckebosch *et al.* (2011) and Syed *et al.* (2006) are as summarized in Table 5, have a considerable improvement in the quality of biogas produced. Factors that were considered were cost, efficiency and environmental effects of byproducts. Biogas purification from acid gasses CO_2 and H_2S using water scrubber reduced more H_2S than CO_2 because H_2S dissolves better than CO_2 in water with the RE of 38.6% H_2S and 21.2% CO_2 (Islamiyah *et al.*, 2015). Water scrubbing had shown significant removal efficiency of H_2S and CO_2. However, this method had performed poorly due to gas leakage from the scrubber.

In another study using soil filtering characteristic, it was observed that the H_2S removal efficiency was almost 100% at all gas flow rates for Allophonic soil, Brown soil and Black sand, followed by Typic sand (around 90 - 100%) (Pham *et al.*, 2019). The study showed that a selection of New Zealand soils with high iron content could potentially be used to construct inexpensive and straightforward H_2S adsorption beds to enhance biogas quality. The H_2S removal efficiency of used soil materials can be improved by exposing them to the atmosphere which adds to the formation of iron oxide which reacts with H_2S. Also, results from Kandola *et al.* (2018) showed that volcanic ash can also be used as a component for the removal of H_2S and NH_3, with the removal efficiency of 80% for H_2S and 100% for NH_3. Moss plant like any plant absorbs CO_2 and releases O_2 to the atmosphere. Due to its large volume to surface ratio, the level of O_2 released is expected to be high in comparison with CO_2 absorbed thus leading to the formation of the oxide. Moss plants as shown grow mostly in a waterlogged environment; therefore, traces of CO_2 and H_2S are expected to be absorbed in this environment. Measuring the net exchange of CO_2 at the surfaces of three dark feather moss and three exposed sphagnum moss sites in a black spruce forest, photosynthesis by moss accounted for 10 to 50% of whole-forest gross CO_2 uptake measured simultaneously by eddy co-variance (Goulden *et al.*, 1997). Various biological methods for the removal of H_2S by biotrickling filters, biofilters and scrubbers from emission sources of industrial and agricultural have been experimented and studied by Chung *et al.* (1996) and Jensen *et al.* (1995), their main setback has been more extended adaptation period of (> 7days) and lower oxidative rates (Yang *et al.*, 1994).

Table 5: Advantages and disadvantages techniques for biogas purification

Technology	System	Advantages	Disadvantages
Physical	Adsorption on activated carbon	High removal efficiency Low operation temperature High loading capacity	Expensive investment and operation CH_4 losses H_2O and O_2 needed to remove H_2S
	Membrane separation	Removal of >98%, CO_2 is also removed Light in weight	Expensive operation and maintenance (fouling problem) Complex
	Water scrubbing	Cheap when water is available (not regenerative) CO_2 is also removed No special chemicals requirement. Easy in operation.	Difficult technique Clogging of the absorption column possible due to bacterial growth. High consumption of water (if there is no regeneration) CH_4 losses
Chemical	Caustic soda	Low electricity requirement Smaller volume, less pumping, (compared to absorption in H_2O) Low CH_4 losses	Expensive investment & operation More difficult technique Not regenerative

Technology	**System**	**Advantages**	**Disadvantages**
	Iron salts	Cheap investment Low electricity and heat requirements Simple operation and maintenance No air in biogas	Low efficiency Expensive operation (iron salt) Changes in pH/temp not beneficial for the digestion process Correct dosing is difficult
Biological	Internal desulfurization	Cheap investment Low electricity and heat requirements, No extra chemicals or equipment required Simple operation and maintenance	Concentration H_2S still high Excess O_2/N_2 in biogas implies difficult upgrading or additional cleaning Overdosing air results in explosive mixture
	External single stage	Simple, flexible design Low capital Low operation and maintenance costs	Difficulties in controlling the operational parameters clogging dilution with the inert N_2 gas and excess O_2 Explosive risk
	External two stage	More than 99% removal efficiency No risk of N_2 and O_2 mixing with biogas	Complex High capital and operational costs

2.9 Biofiltration Design and Operating Parameters

Biofiltration refers to the treatment of waste air or water using biological technologies. Biofilter can be defined as a layer of biologically active media, usually of natural origin. The composition of filter particles is mostly soil, compost, peat, wood chips, tree bark and heather (Sercu *et al.*, 2006). According to Delhoménie *et al.* (2005) biofiltration design can be of two types; open designed biofilter and enclosed design biofilter. The difference between the open design and closed is the surface area and direction of the flow of gas. With the open design, it requires a large area with only ascending gas flow and is usually installed outside. While with a closed design, the volume is more restricted and can have either ascending or descending inlet gas flow. Some of the main advantages of using biofilter include low operating costs and have less impact on the environment which is attributed to their self-containment. The disadvantage includes the high pressure drops, less suited when the concentration of contaminants is too high and deterioration of the packing material over time.

It has also been reported that over time clogging may occur due to the difficulties to control moisture, pH and accretion of excess biomass in the packing material (Devinny *et al.*, 2017; Mannucci *et al.*, 2012). The effectiveness of a biofiltration unit depends on various factors; microbial population, type of material used for packing and type of enrichment during the inoculation process. Each factor plays a vital role in elimination capacity, removal efficiency and overall outcome of the removal. Once the biofilter becomes operational, the performance efficiency depends on temperature, moisture content, pH, flow rate, containment loading rate and structure (Kim *et al.*, 2008). The influence of each parameter is described hereafter.

2.9.1 Temperature

A packed bed is mainly governed by the difference in temperature between the inlet gas and the outdoor air. The heat generated by exothermic biological reaction tends must also be taken into account. According to Wani *et al.* (1999), optimum operating temperature for biofiltration applications is around 35 - 37˚C but in most cases, biofilters operate at a temperature range of 20 - 45˚C (mesophilic range). With the use of microbial organisms, the temperature must be consistent with microbial requirements. For example, Thiobacillus denitrificas and Thiobacillus novellus tend to thrive mostly in the temperature range 10 - 39˚C with an optimum range of around 28 - 35˚C (Vlasceanu *et al.*, 1997).

2.9.2 Moisture Content

Moisture content in the packed bed biofilter (bioreactor) is optimum at around 40 – 50% as studied by López *et al.* (2012). It is essential for the survival and metabolism of the resident microorganisms and improves the filters buffer capacity which enables microbial growth. Excessive moisture can lead to pressure drops, bed desiccation and the formation of anaerobic zones, whereas less moisture leads to a significant drop in removal efficiency. According to Delhoménie *et al.* (2005), the factors affecting the bed moisture content includes;

(i) Inlet relative humidity

(ii) Water holding capacity of filtering material

(iii) Gas flow rate through the bed

(iv) Exothermicity of the reaction which tends to desiccate the bed

2.9.3 pH Condition

During biofiltration of H_2S oxidation by most bacteria and solubility of H_2S in water can cause a pH decrease and hence acidic environment. In some cases where the efficiency of H_2S removal is affected due to a decrease in pH, a buffer solution is added. In general, microorganisms have a specific optimum range of pH for their metabolic activities: pH 5 – 9 for bacteria and pH 2 – 7 for fungi. The range of pH in most compost beds is between 7 and 8, which is typically preferred by most microorganisms (Shareefdeen, 2005).

2.9.4 Nutrient Supply

Carbon, energy and nutrients (nitrogen, potassium, phosphorus and trace elements) are essential for microbial growth. Organic packing materials, such as compost, tend to have these nutrients. However, during operation with time, these nutrients are gradually depleted (Dumont, 2015).

2.9.5 Pressure Drop

The bed pressure drop is an important parameter in biofiltration it has to be taken into account during estimation of operation costs. Leson *et al.* (1995) reported that there was an increase in energy demand from 7 to 25 kW when the pressure drop increased from 4 to 25 cm of water within 6 months of operation. Factors that can cause a pressure drop in biofilters include; packing materials, gas velocity (flow rate), biomass growth and biofilter dimensions. The effect of pressure drop in the biofilter includes, clogging, creation of anaerobic zones and can in turn affect the overall performance (Devinny *et al.*, 2017). In a long biofilter operation, the increase in pressure drop due to extra biomass and bed compaction decreases the biofilter efficiency, which signifies a major drawback of biofiltration. Naturally, bioactive media such as; soil, compost, or peat contain microorganisms that have been studied to show biodegradability of contaminants. Therefore, they have been effectively employed in bioremediation of contaminated sites.

As the result, it led to the development of soil biofilter, in which soil with low clay and high organic carbon content is packed in a bed and contaminated air passes through the soil bed to biodegrade the air contaminants. Soil biofilter (soil compost reactor) are filtering systems whereby beds of material are arranged such that perforated pipes can deliver the discharge air, as it passes through the moist, aerated biological material. At this stage, the pollutant gases adhere to the soil particles by either dissolving them into soil solution or by exposing them to microbial digestion (Nelson *et al.*, 2011). The soil contains physical and chemical characteristics to support pollutant removal and microbial activities.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Equipment and Accessories

LZB-3WB Gas rotameter, (Mill Gas counter, Ritter Biogas-meter), Geotech Biogas 5000 Gas analyzer, Sleeve, Moss plant sample from the same location, gravels and pebbles, Polyplastic container (25 cm × 16 cm × 9 cm), soil samples, Grinder, plastic containers for soil and moss sample collection and Biochar to help reduce mold and odor in the filter.

3.2 Sample Collection and Preparation

The soil samples and profile statistics were collected from Tanzania Agricultural Research Institute located in Tanga, Tanzania, as part of the soil survey profile for Kwaraguru Sisal Estate. In total, four soil samples were identified as likely candidates for evaluation based on guidelines for soil classification World Reference Base for Soil Resources 2014 Edition (World Reference Base, 2015) in naming and creating of soil map legends. The moss substrate was collected at the campus as it was during the rainy season since they were easily spotted.

Soil survey database and profile information are presented in Table 6. The selected soil sample contained a high number of metallic micronutrients per kilogram (the amount of metallic nutrient a plant can absorb via its roots), percentage of soil organic carbon and carbon to nitrogen ratio. The soil samples with the high composition of extractable micronutrients (Fe, Zn, Cu and Mn) from each profile were selected for this study. Exchange Cu mg/kg refers to 1 mg of exchangeable copper that can be absorbed by the roots in 1 kg of soil as nutrients. Other properties, including the percentage of organic carbon %C, carbon to nitrogen ratio C/N and pH, were also considered for the selection. The selected soils were named T1, T2, T3 and T4.

Table 6: Soil database and profile information

Parameters	Coordinates (Lat-Long)			
	-5.42057°S, 38.52185°E	**-5.42519°S, 38.52794°E**	**-5.48036°S, 38.52422°E**	
Appearance	Dark reddish-brown	Very dark greyish brown	Dark reddish-brown	
Sample name	T1	T2	T3	T4
Depth (cm)	0-15/20	20/25-40	0-15/20	15/20-40
Clay %	62	40	50	58
Texture class	Clay	Clay	Clay	Clay
Bulk density g/cm^3	1.02	1.34	1.18	1.21
pH H_2O	5.2	6.9	5.4	5.4
Exch. Cu mg/kg	7.47	7.77	2.25	1.5
Exch. Zn mg/kg	0.99	0.48	1.62	0.36
Exch. Mn mg/kg	16.5	47.1	117.0	39.3
Exch. Fe mg/kg	33.99	31.29	51.39	57.69
Organic C %	1.49	1.36	1.77	1.10
C/N	6.77	4.69	8.05	6.47

3.3 Filter Preparation

To construct a prototype of the filter, each substrate i.e. soils T1, T2, T3 or T4, biochar and moss was pretreated after collection, to remove unwanted components like roots, plastics and leaves. The filter was designed to provide a high specific surface area for gas reaction with a low-pressure drop over the packed column. A combination of a high content of active ingredients favors a substantial sulfide binding capacity (Skerman *et al.*, 2017). Each filter contained one of four types of soil (T1, T2, T3 or T4) sieved at less than 400 µm with variable mass (100 g, 150 g or 200 g); 100 g of biochar (charcoal) dust sieved at less 350 µm and 545 g of naturally grown moss plant collected from the damp sidewalk during the rainy season. The packed bed arrangement of the substrates was adopted from Pham *et al.* (2019), the study demonstrated the removal of H_2S using local soil materials from biogas produced by anaerobic digestion of animal wastes. In this study, 700 g layer of small and medium gravels was added above the aerator to prevent blockage by overlying filter material. Moss plant was added as a top layer, with soil and biochar dust as preceding layers below it in order to ensure active gas exchange, growth and sustainability of the filter. The substrates were packed into poly-plastic containers each with the dimensions (25 cm × 16 cm × 9 cm) with an airtight cap to cover the top part; the container was transparent to allow just enough light in the filter to aid photosynthesis reaction of moss plants.

An inlet port for the introduction of unpurified gas was inserted at the bottom part connected to the aerator (20 cm long) to ensure homogeneous distribution of the inlet gas across the face of the bed. A step by step preparation of the filter is as shown in Fig. 4.

1- Inlet through aeration

2- Gravel packs (200 g)

3- Biochar dust (250nm/ 100g)

4- Soil substrate (100 g)

5- Moss substrate (545 g)

6- Filter open

Figure 4: Preparation of the biofilter

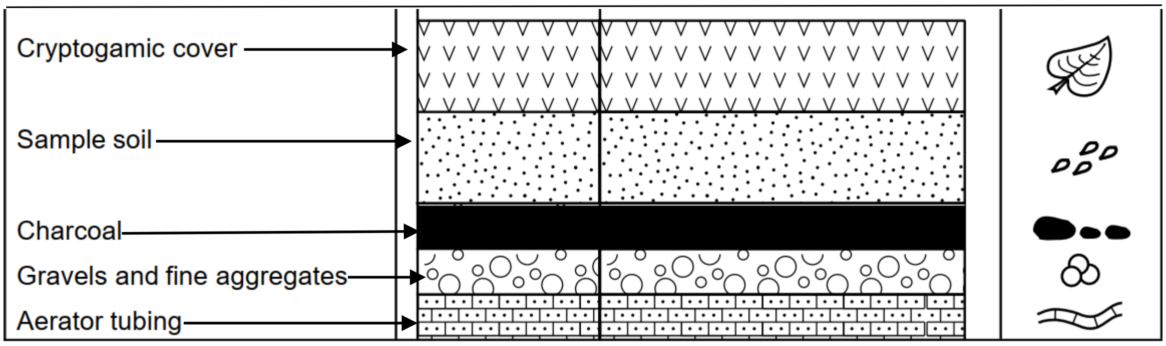

Figure 5: Schematic diagram of substrates arrangement in the filter

The bed included soils with a high amount of micronutrient content and %C, biochar dust (charcoal) which contains unmodified activated carbon and moss substrate. The substrates were arranged in layers based on the role of each substrate in gas sorption efficiency and regenerative capacity. Filter fabrication was conducted at room temperature to ensure all the humid condition present in the moss plant is preserved.

The humid condition in the filter is essential to ensure microbial action and enhance the sorption of CO_2 and H_2S. Xie *et al.* (2017) showed that the presence of soil moisture content results in increased removal capacity for H_2S in a soil biofilter. The presence of water has also shown a beneficial effect on the overall temperature catalytic performance of activated carbon for the oxidation of H_2S to sulfur (Primavera *et al.*, 1998). After fabrication, the filter was then closed and sealed to begin measurements. It was designed to require no energy during its operation.

3.4 System Operation

Two biogas reactors L1 and L2 available at private premises were used for experimental testing of the biofilter. Table 7 depicts the features of both digesters as well as the average composition of raw biogas which was comparable by methane and carbon dioxide contents but slightly different by ammonia and hydrogen sulfide concentrations. In our on-site tests, biogas flow was allowed to pass through the filter media contained in a rectangular plastic container. The block diagram of the experimental set up is shown in Fig. 6. The on-site set up during the experiment is as shown in Appendix 1.

Table 7: Domestic biodigesters used for the analysis

Digester type	Digester volume (m^3)	Feedstock	Volume gas column (m^3)	Max pressure (mbar)	Raw gas composition
L1	16	Domestic sewage and garden wastes	4	107.8	68–72% CH_4, 38 – 40% CO_2, 6 – 14 ppm NH_3, 498 – 913 ppm H_2S
L2	9	Rougher garden wastes and overflow from L1	0.8	84.3	64–66% CH_4, 34 – 38% CO_2, 3 – 7 ppm NH_3, 80 – 110 ppm H_2S

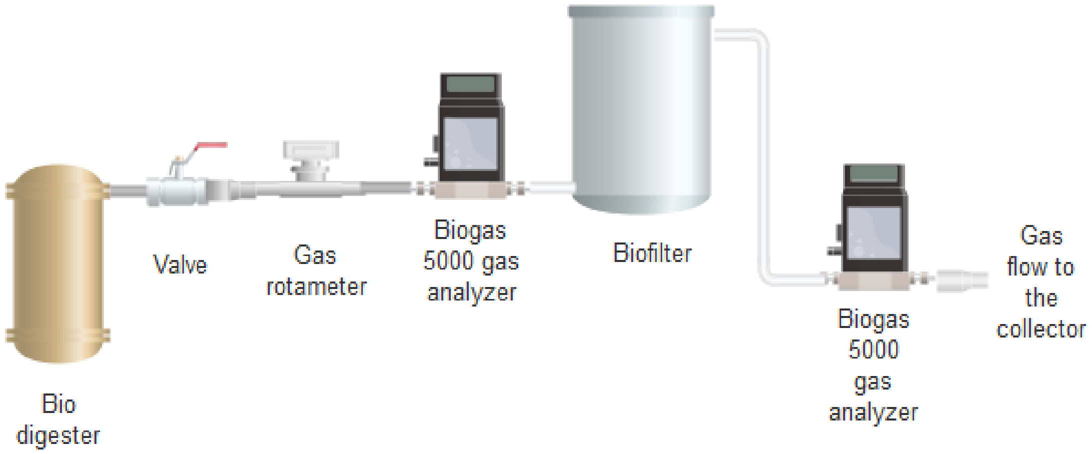

Figure 6: Photo and schematic diagram of the experimental setup

The gas flow rate was controlled using the gas regulator and LZB-3WB rota-meter. The gas composition was recorded before and after the filter using a portable gas analyzer (GA5000 gas, Geotech, England). The overall pH of the filter measured before the experiment was 6.8. Experimental analysis by Nelson *et al.* (2011) revealed that for the regular operation of soil-based biofiltration for air purification, the pH levels should be maintained at around 7 to 8, to prevent the formation of acids from the degradation of inorganic gases.

The tests were divided into three parts. The first part was conducted to analyze the effect of soil type on biogas purification to determine the sorption capacity of the adsorbents. The second part was aimed to analyze raw gas adsorption by each substrate and the third part was to summarize the role of each adsorbent in gas purification which was conducted with flow rates of 80 and 100 ml/min during times 0-150 min for each filter in ambient condition. The arrangement of these substrates in the filter is as shown in Fig. 5.

To examine the performance of each substrate in a filter, raw biogas was allowed to pass through a 5 g sample packed in airtight 5 ml plastic tube at a constant flow of 100 ml/min, the inlet and outlet concentrations H_2S, CO_2 and NH_3 were measured and the readings were recorded in a 10 min interval for 80 min. A small sample mass had to be used to ensure the maximum surface area for adsorption and to avoid a very high-pressure drop which is not recommended for biofilter operation. For example, Abatzoglou *et al.* (2009) reviewed from various studies that commercially packed biofilters are engineered to provide high specific surface area, having a low-pressure drop and together with a high content of active ingredient, provide high sulfide binding capacity.

3.5 Filter Performance Parameters

The performance of the developed biofilter was determined in terms of removal efficiency (RE) and sorption capacity (SC). The CO_2, NH_3 and H_2S concentrations of treated gas at the outlet were analyzed at 10 min intervals for each test, RE and SC were calculated using Eq. (3.1) and Eq. (3.2) respectively. Whereby C_i and C_f are the initial and final concentration of H_2S (CO_2 or NH_3) as measured before and after filtration respectively; Q is the flow rate ($m^3 \cdot h^{-1}$), M is the atomic mass of sulfur, Vmol is the molar volume of the gas ($L \cdot mol^{-1}$) under standard conditions. A breakthrough time (BT) in hours was recorded as the time when C_f approached 50% of C_i, where no significant adsorption of sulfur by the substrate was observed.

$$\text{RE (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ldots\ldots\ldots\ldots\ldots\ldots \text{(1.1)}$$

$$\text{SC} \left(\frac{g\, sulfur}{100g\, sorbent}\right) = \text{Q} \times \frac{M}{Vmol}\left(C_i - C_f\right) \text{BT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3.2)}$$

To elucidate the role of each substrate, special tests were conducted as described in Section 3.4; the SC of each biofilter component was calculated by using Eqn. 3.2. Where C_i and C_f are the initial and final concentration of H_2S, CO_2 or NH_3 as measured before and after filtration respectively; Q is the flow rate ($m^3\ h^{-1}$), M is the atomic mass of sulfur, V mol is the molar volume of the gas ($L\ mol^{-1}$) under ambient conditions. A breakthrough time (BT) in hours was recorded as the time when C_f approached 50% of C_i, where no significant adsorption of sulfur by the substrate was observed.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Soil Type Effect on Biogas Purification

Different types of soil, T1, T2, T3 and T4, of the same soil mass 100 g were tested in biogas purification at a constant flow rate of 80 ml/min. The masses of other substrates,100 g of biochar and 545 g of moss, were kept constant during fabrication of the filter. The biogas composition before and after the filter was monitored every 10 min for 150 min.

The results as depicted in Fig. 7 illustrates the removal efficiency for CO_2, H_2S and NH_3 from each soil type at a constant flow rate with the initial concentrations, as shown in Table 7. This was conducted to determine the filter that showed a high percentage on average for the removal of all these impurities. The results indicate that filters with T3 and T4 soils had the most substantial average removal of CO_2 at 76% and 75% respectively. T3 filter also showed a significant RE of NH_3 at 72% on average over the entire period than other soil types. For H_2S removal filters T4 and T3 showed the largest RE at 97% and 93% respectively. The reason for higher RE exhibited by soils T4 and T3 is the highest total content of extractable iron compared to T1 and T2, as shown in Table 6. As it has been demonstrated in Eqn. 2.3 high iron content in the soil contributes to more significant interaction with H_2S impurities. Presence of other extractable micronutrients (Zn, Cu and Mn) also favors in reacting with H_2S.

The test results accord well with an investigation Rodriguez *et al.* (1998) where it was shown that H_2S and S_2 reacted faster with CuO, ZnO than corresponding sites of alumina (Al_2O_3) based on the bandgap size and chemical reactivity. Also, it was further observed by the test results accord well with an investigation Rodriguez *et al.* (1998) where it was shown that H_2S and S_2 reacted faster with CuO, ZnO than corresponding sites of alumina (Al_2O_3) based on the bandgap size and chemical reactivity. Iron-rich and zinc-containing soils effectively removed H_2S from coal-derived natural gas (Ko, 2008; 2011). The soil T3 showed higher interaction with H_2S.

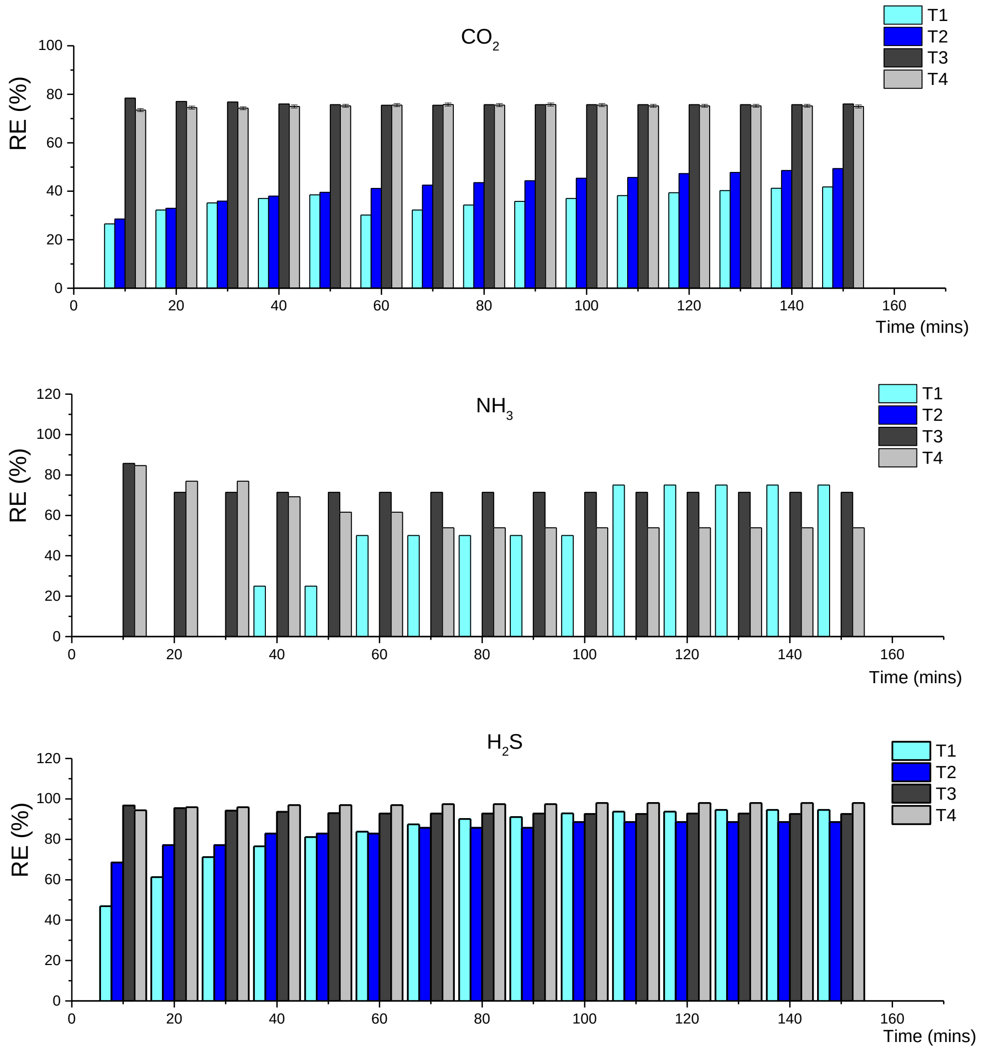

Figure 7: Biogas purification by filters with different soil samples: RE versus operating time. Test conditions: Q = 80 ml/min, m = 100g, T = 19°C, C_0 = 36.4% for CO_2, 13 ppm for NH_3, 836 ppm for H_2S

Table 8: **Soil types performance in biogas purification, RE, average over operating time (Q = 80 ml/min)**

Gas analyzed	**Initial concentration (Ci)**	**RE, %, average over time 2.5 hrs**			
		T1	**T2**	**T3**	**T4**
CO_2	36.4 – 40.0%	36.0	42.0	76.1	75.1
NH_3	7 - 13 ppm	56.3	nd	71.4	56.4
H_2S	498 - 836 ppm	83.5	84.0	93.3	97.1

**nd – not determined.*

The dark reddish-brown coloration of the soil indicates richness in the crystalline structure of iron oxide minerals which have a strong influence on H_2S removal capacity (Skerman *et al.*, 2017). Also, Lasocki *et al.* (2015), observed that the iron oxide present in soils and activated carbon (charcoal) as beds in filters reduced almost 100% of H_2S in a 30 min exposure period in the Laboratory-scale investigation. Other factors that contributed to better performance of T3 soil were high levels of soil organic matter, organic carbon percentage and C/N ratio of the soil compared to other soils. The presence of organic matter improves soil aggregate and structural stability which are significant for infiltration of water and aeration into the soil, thus enabling the high surface area of reaction (Lefèvre *et al.*, 2017). Soil organic carbon is vital in improving soil structure and provides habitat for soil biota, which together ensures sustainable yields as they retain water and nutrients (Lal, 2009; Lorenz *et al.*, 2007). The level of C/N in the soil determines the rate of decomposition of organic matter and soil productivity, which was studied by using paddy fields by Li *et al.* (2016). Therefore, T3 soil was subjected to further tests in the effect of soil mass and flow rate to the removal efficiency.

4.2 Effect of Varying Soil Mass on Removal Efficiency

Further tests were performed to identify how the mass of the soil affects the removal of CO_2, NH_3 and H_2S from raw biogas. The experiment was conducted only T3 soil, which exhibited better results than other types of soils. The masses of other substrates and flow rate were kept constant at 100 ml/min. The filters that differed in soil masses were used, whereby; T3–100, T3–150 and T3–200 referred to T3 soil substrate with a mass of 100, 150 and 200 g respectively. The initial concentration of raw gas was in the range of 36.4 – 37.5 % for CO_2, 7 - 13 ppm for NH_3 and 498 - 836 ppm H_2S. Soils had the same particle size of <400 µm.

During operation time of 150 min, the outlet impurities were recorded as the raw gas passed into the filter. Figure 8 shows the removal efficiency of CO_2, NH_3 and H_2S gases. For CO_2, the removal efficiency was approximately 99.7% for T3 – 200 over the operation time. When the mass of the soil was further lowered to 150 g, the removal efficiency dropped to about 75% and further to nearly 70% for the filter with 100 g soil.

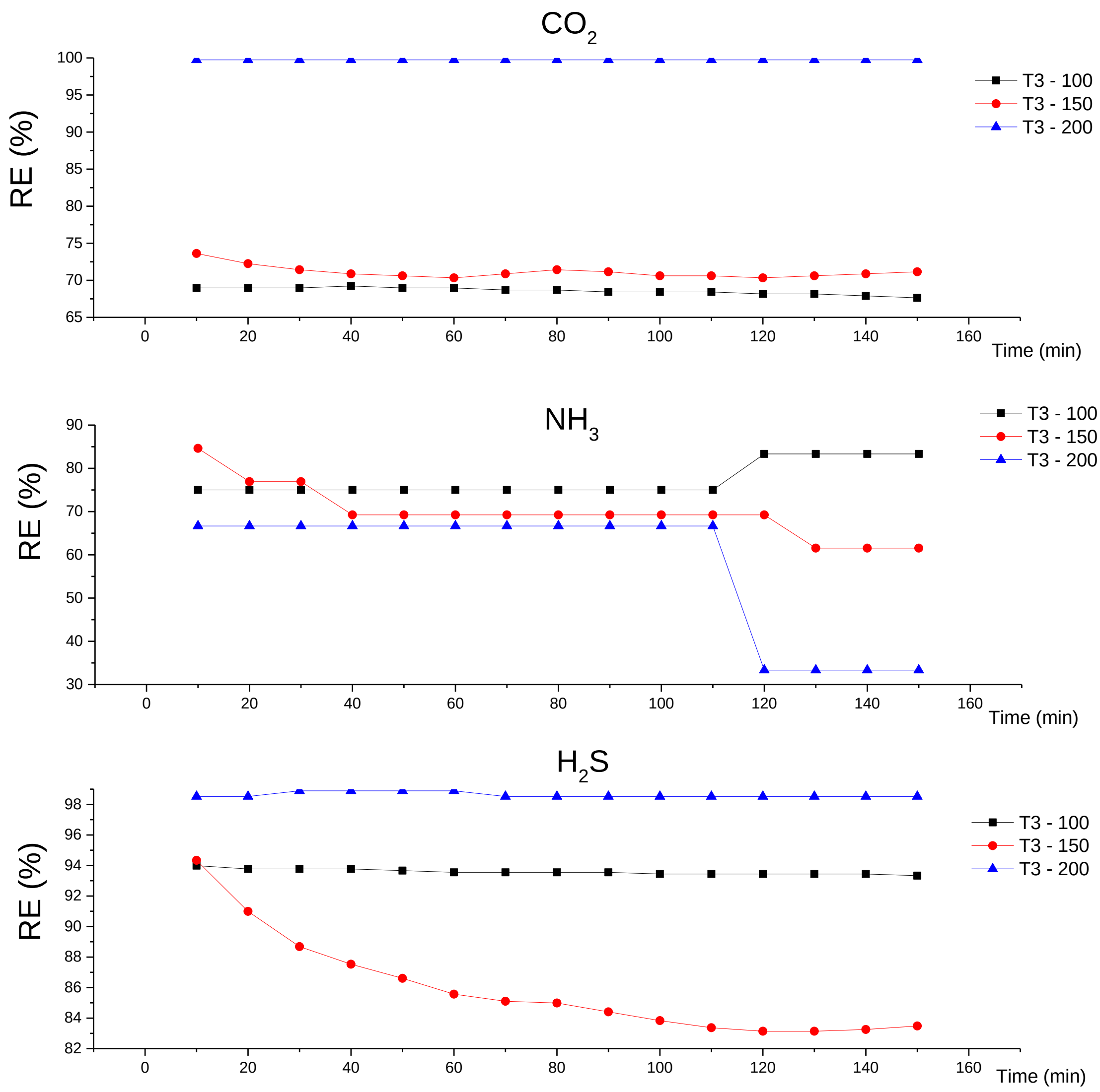

Figure 8: Soil mass effect of the filter T3. Test conditions: Q = 100 ml/min, m_1 = 100 g, m_2 = 150 g, m_3 = 200 g P = 10 kPa C_0 = 37.5% for CO_2, 13 ppm for NH_3, 836 ppm for H_2S

For the case of NH_3; RE was 83% but dropped to 33% for T3–200 and as high as 83% to 77% drop for T3–150. The filter T3-100 had a maximum RE of 80% before saturation. After 120 min, no more NH_3 adsorption was observed. It is supposed this sharp decrease could be due to the drop in the initial concentration of the gas to the lowest amount recorded of 7 ppm and that low ammonia concentration measurement occurred at the sensitivity limit of the gas analyzer. Filter T3–100 has a large surface area of reaction, unlike other filters with substantial mass, which are highly compacted thus having less adsorption rate.

As it was demonstrated by Kent *et al.* (2000), filter beds with small particles size offer a high specific surface area for reaction and thus favoring nitrification and microbial activity, but also they tend to constitute a greater resistance to gas flow which increases as biomass grows in bed porosities (Yang *et al.*, 1994). On the other hand, large particles have low-pressure drop since the gas flow is not blocked, but offer fewer surface sites for oxidation reaction, therefore it can lead to lower elimination performances (Delhoménie *et al.*, 2002). Also, NH_3 has a low Henry's constant ($H_{20^\circ C} = 5.6 \times 10^{-4}$) (Perry *et al.*, 2008) and a protonation constant $pK_{a,}$ 20˚C of 9.23 (Weast *et al.*, 1984). These values make NH_3 in biofilters to be partly retained onto the surface of carrier material by adsorption and by absorption of water fraction of the material (Sercu *et al.*, 2006).

The T3–100 filter showed higher RE in H_2S than T3-150 and T3–200, which can be explained by the availability of high surface area of adsorption between the gas molecules and the soil adsorbent containing a high content of iron and other cations eg Cu and Zn. Filter T3-200 due to a large mass of soil content has the higher gas retention time of all the filters, as it takes longer for the gas reaction to complete. The large mass of soil may also lead to clogging. It can be effective if the soil is evenly dispersed to allow more gas retention time. The higher retention time was effective in H_2S elimination capacity as it was studied by Yang *et al.* (1994).

From the results, one can conclude, that with T3–100, there was a steady flow of raw gas from the aerator to the subsequent layers, thus having quick reaction time and a greater RE for H_2S and NH_3. On the other side, a large mass of soil causes the filter to be non-porous since the particles are tightly compacted together, resulting in the reduced surface area of reaction and large pressure drop.

4.3 Effect of Biogas Flow Rate on the Biofilter T3 Removal Efficiency

The H_2S, CO_2 and NH_3 removal were further analyzed for filter T3 by considering variation in flow rates of 80 ml/min and 100 ml/min. The filter performance with the soil mass 100 g (T3-100) is shown in Fig. 9. As is seen, quite steady RE behavior is upheld for all three impurities; except a small and casual variation for NH_3 that can be attributed to a small but changeable amount (7–13 ppm) in the raw gas. The CO_2 removal is affected by the flow rate; the RE lowered by 7% from 80 to 100 ml/min. In the case of H_2S, the change of flow rate practically does not influence the RE that remains constant ≈94% during the filter operating time. A summary of removal efficiency at both flow rates is given in Table 8. Also, the effect of the soil mass is taken into account.

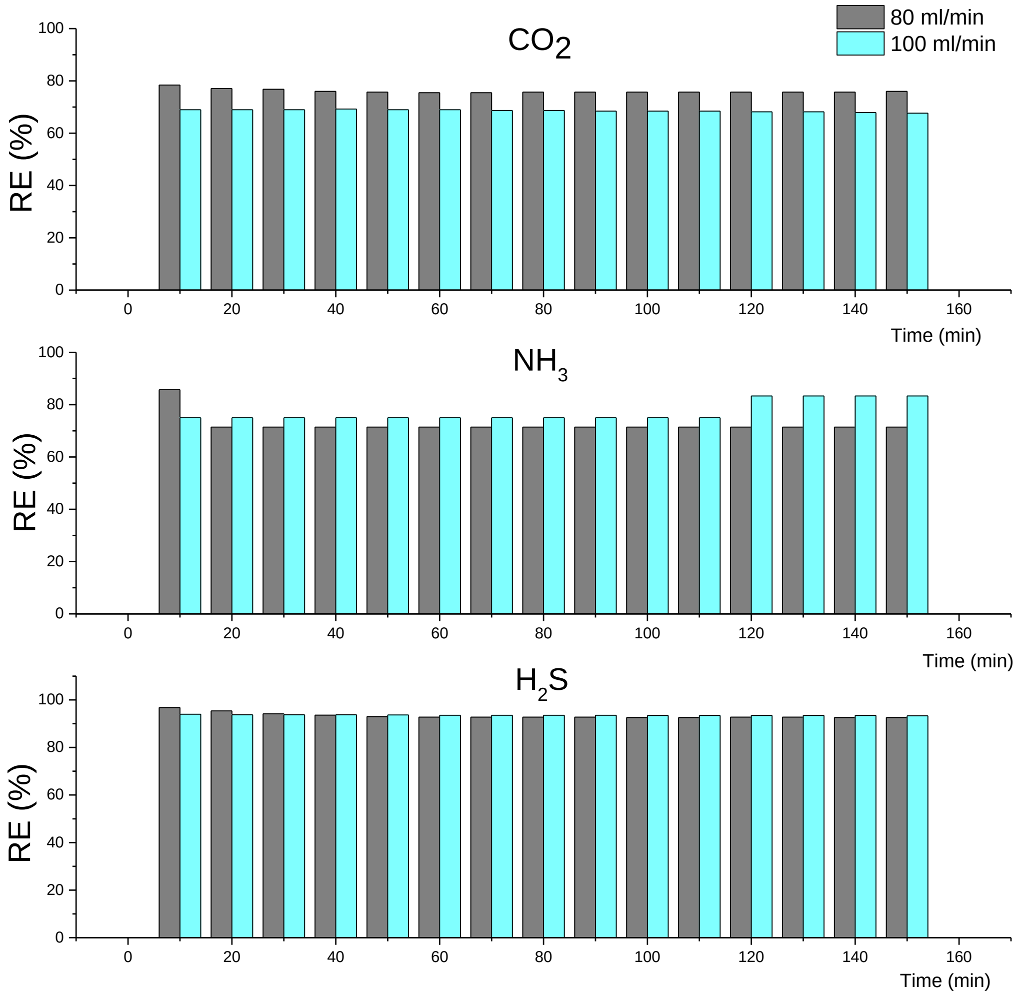

Figure 9: RE of the filter T3–100 at two different flow rates (80 and 100 ml/min). Test conditions: Q_1 = 80 ml/min, Q_2 = 100 ml/min m = 100 g, P = 10 kPa, C_0 = 37.7% for CO_2, 12 ppm for NH_3, 915 ppm for H_2S

The RE for CO_2 was high for the filter with the largest soil mass at both flow rates. This can be attributed to the effect of pressure drop. The pressure drop is high for the most substantial packed bed in comparison to other filters. This, as a result, makes CO_2 concentration as it passes through the packed material in a given time to be significantly low, thus allowing time for maximum adsorption of the gas by the moss substrate. The same can be explained for the RE of CO_2 to be higher for the same flow with T3-150 than T3-100. Meanwhile, with a low flow rate for T3-100 and T3-150 filters, high RE is observed. This can also be as a result of having sufficient reaction time for the adsorption of CO_2 by the substrate.

Table 9: Effect of soil mass and biogas flow rate on the biofilter T3 performance; H_2S removal efficiencies are given as average values over 2 hours operating time

Gas analyzed	Initial concentration (Ci)	Flow rate, (Q, ml min^{-1})	RE (average over time), %		
			T3-100	T3-150	T3-200
CO_2	36.4 – 40.0 %	80	76.1	75.9	99.7
		100	68.6	71.1	99.7
NH_3	7 - 13 ppm	80	72.4	73.3	50.0
		100	77.2	69.7	57.8
H_2S	498 - 836 ppm	80	93.3	97.7	96.7
		100	93.6	85.9	98.6

On average, the RE for NH_3 is high with T3-100 at 100 ml/min and drops as the mass of the filter increases (T3-150>T3-200). Moreover, with the flow of 80 ml/min, there is a slight difference in RE for T3-100 and T3-150, but it drops for T3-200. Joshi *et al.* (2000) demonstrated on a field-scale peat biofilter that NH_3 removal along with sulfur compounds can also be attributed to the adsorption by the acidic nature produced during oxidation of sulfur compounds.

An increase in the flow rate, results in the increase of gas reaction time for the filter with larger mass (T3-150 and T3-200) and lower risk of clogging. But for the filter with a small mass, the effect is reversed as more gas will pass through without been adsorbed by the soil adsorbent. For the T3-100, the RE was considerably high for a low flow rate than a high flow rate. This allows a large number of particles present to interact with H_2S gas, offering more time for oxidation to occur. With a low flow rate, maximum gas reaction time was observed. These results are in agreement with studies from Chung *et al.* (1996) and Singh *et al.* (2011), whereby, data on H_2S removal by combined chemical and microbial solution, showed that RE for H_2S increased with increasing gas reaction time. In the investigation on operational parameters of biofiltration design by Yang *et al.* (1994), it was observed that an increase in loading rate results in to decrease in gas retention time, due to insufficient reaction time between H_2S molecules and the biomass in the filter.

Thus, H_2S RE can be improved by either reducing the flow rate or increasing the soil volume. As seen in Table 9, the best performing filter for all gases by considering average RE was T3-100. Other filters showed better RE for one type of pollutant but less for the other type measured at either of flow rates. For example, T3-200 showed high RE for CO_2 and H_2S but less with NH_3.

4.4 Analysis of the Function of each Substrate

4.4.1 Sulfur Adsorption Performance of Various Adsorbents

The breakthrough time is used to specify the saturation time of the substrate before it needs regeneration or replacement. Longer breakthrough time implies a better adsorption capacity of the particular substrate (adsorbent) (Chowdhury *et al.*, 2012). It also implies a shorter reaction time. Variations of the adsorbate concentration against the operating time of a filter are known as breakthrough curves (Sethupathi *et al.*, 2017). These curves are presented in Fig. 10a for different biofilter substrates, the soils T3, biochar and moss. The sample was considered saturated when the outlet concentration reached 50% of the inlet.

The H_2S breakthrough time for adsorbents T3 and T4 was both about 80 min, after which it was observed, a minimal variation in sulfur adsorption. Also, for the case of biochar and moss, the H_2S breakthrough time (BT) was 50 min and 20 min respectively. For other adsorbents, T1 and T2, a small change in their concentrations were observed, thus no significant adsorption was detected. The adsorption breakthrough time of T3 and T4 was higher than other adsorbents (substrates). A comparison between initial and final H_2S concentrations is shown for the substrates in Fig. 10b. The sulfur sorption capacity of each substrate was calculated using Eqn. 3.2 and indicated as the amount of sulfur adsorbed per 100 g of the sorbent in Fig10c. As seen, the soils T3 and T4 retain the highest H_2S amount, 20.8, 20.1 g-S/100 g respectively, compared to other adsorbents whereas T1 and T2 soils are practically unable to adsorb sulfur. Regarding biochar and moss substrates, H_2S was partly retained with a sorption capacity of up to 6.0 and 1.8 g-S/100 g respectively. The results are comparable with data by Sahu *et al.* (2011) whereby, the sorption capacity of red mud (RM) sample used for H_2S removal was 2.1 g-H_2S/100 g of RM. High sorption capacity by T3 and T4 is comprehensible, as they both have a high total content of extractable cation, specifically iron and high C/N compared to other soil substrates as shown in Table 6. Summarizing contributions from the three substrates; (soil T3, biochar and moss), the designed SC biofilters T3-100 and T4-100 can be estimated to remove a total of 10.8 and 10.7 g-S respectively.

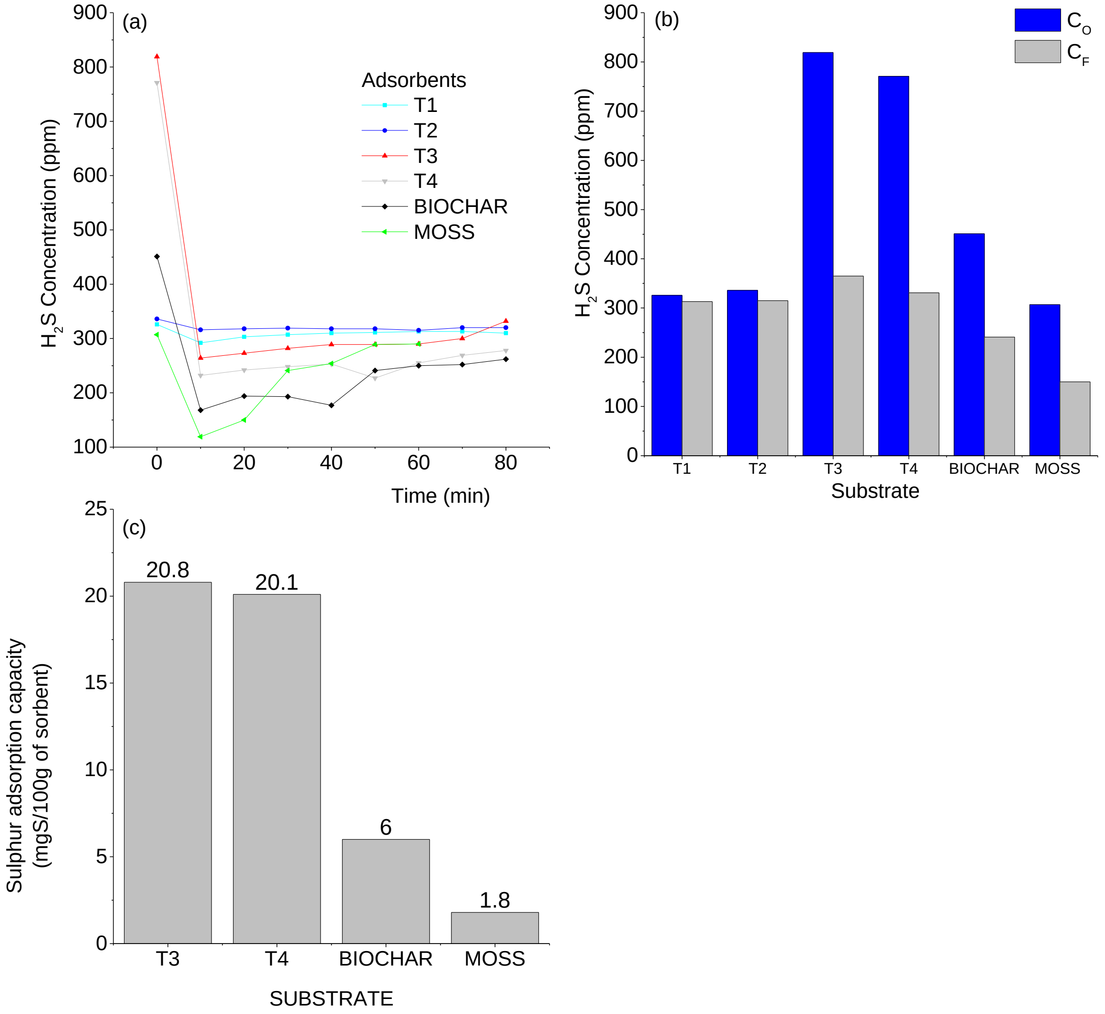

Figure 10: Sulfur removal by various adsorbents: (a) Breakthrough curves, (b) H_2S absorption over breakthrough time and (c) Sorption capacities. Test conditions: Q = 100 ml/min, m = 5 g, C_0 = 307-819 ppm for H_2S, Time = 80 min

4.4.2 Moss Substrate Performance in CO_2 and NH_3 Removal

The capacity of a moss substrate on removing CO_2 and NH_3 from biogas was tested under the same conditions as described in the previous sub-section about H_2S sorption. A 59% drop in CO_2 concentration and 38% for NH_3 was recorded during the 60 min of the experiment Fig. 11. For the case of CO_2, moss plants like most cryptogams account for the largest net carbon uptake (photosynthesis minus respiration) from the atmosphere (Chapin *et al.*, 2006; Field *et al.*, 1998). The present study demonstrated moss to be very effective in CO_2 adsorption from raw biogas for 60 min. A low adsorption rate for NH_3 is mainly because moss is non-vascular plant as most ammonia needs to be converted first to ammonium and nitrate by nitrifying bacteria and absorption by the plant from the soil is done by roots (Joshi *et al.*, 2000). The summary of the results is as shown in Table 11.

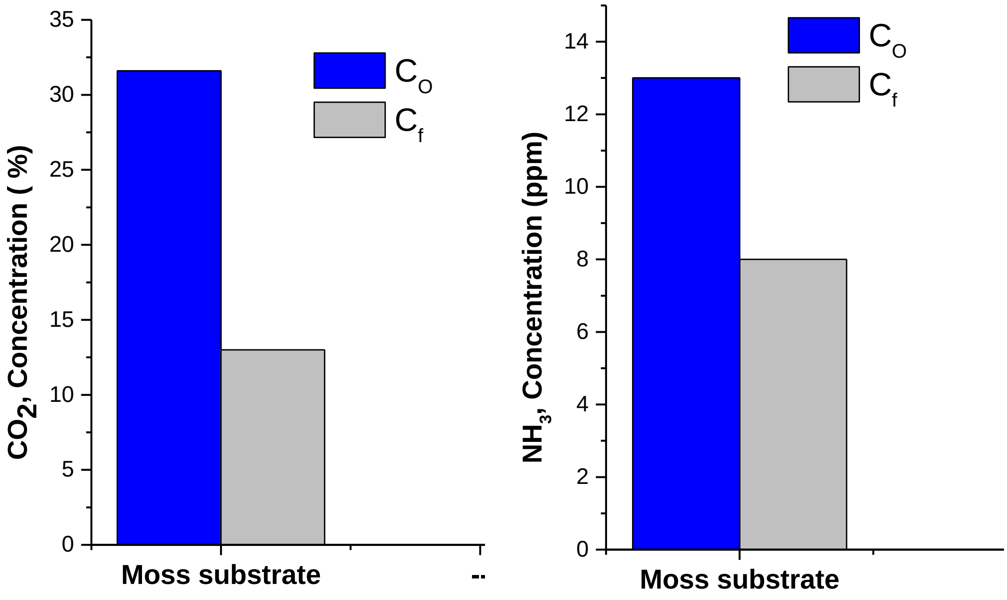

Figure 11: Adsorption of CO_2 and NH_3 by moss substrate in 60 min operation time

Table 10: Summary of BT, SC (g-S/100g of sorbent) for all substrates

Substrate, impurity	**BT, min**	**SC, g-S/100 g sorbent**
T1, H_2S	<10	n/a
T2, H_2S	<10	n/a
T3, H_2S	70	20.8
T4, H_2S	70	20.1
Biochar, H_2S	50	6.0
Moss, H_2S	20	1.8
Moss, CO_2	45	n/a
Moss, NH_3	40	n/a

4.5 Comparison of Biogas Purification with other Biofilters of Different Media

Biological techniques can be the best alternative in the reduction of impurities in the biogas, because the use of chemicals is limited and it is considered economical and environmentally friendly. Investigations of different media for biogas purification in comparison to our study are summarized in Table 12. In this study, NH_3 was removed to up to 77.2% at a constant flow of 0.006 $m^3 h^{-1}$ (100 ml/min). For CO_2 and H_2S removal, the physical and chemical properties of biochar in the filter have significantly improved the adsorption capacity.

Table 11: Absorption properties of the cryptogamic filter compared to other biofilters

Bed type/Adsorbent	**Gas**	**Impurity Gas**	**Loading rate**	**RE (%)**	**Elimination capacity**	**Disadvantage**	**Reference**
Peat biofilter	NH_3	20 ppmv	1.8 g m^{-3}hr^{-1}	80	41 g m^{-3} d^{-1}	Overloads at a loading rate of 7.9 gm^{-3}hr^{-1}. Prone to channeling and maldistribution Limited ability to neutralize acidic degradation products.	Hartikainen *et al.* (1996)
Perlite biofilter	NH_3	20 - 50 ppmv	8.6 g m^{-3} d^{-1} and 21.5 g m^{-3} d^{-1}	99.5	NA	Production of NO and NO_2 at the outlet	Joshi *et al.* (2000)
Compost and activated carbon as added material	NH_3	20 – 500 ppmv	0.2 - 40 g NH_3/kg d^{-1}	95.9	NA	For better removal effluent NH_3 should be <200 ppm.	Liang *et al.* (2000)
Cow manure compost	H_2S	~ 1500ppm	58 m^{3} h^{-1}	80	16 – 118 g m^{-3} h^{-1}	High operating costs, clogging to deposition of elemental sulfur	Zicari (2003)
Chemical scrubber converted to biotrickler	H_2S	30 - 50 ppm	NA	97	38–127 g m^{-3} h^{-1}	High operating costs and further research to reconcile lab-scale and field results.	Gabriel *et al.* (2002)

Bed type/Adsorbent	**Gas**	**Impurity Gas**	**Loading rate**	**RE (%)**	**Elimination capacity**	**Disadvantage**	**Reference**
Metal-ferrite sorbents made from heavy metal wastewater sludge	H_2S	1% H_2S in a mixture of gas.	4000 mL h^{-1} g^{-1}		26.1 g-S/100g by ZF_6 sorbent	High sulfidation temperature and longer breakthrough time	Tseng *et al.* (2008)
Biomass ash	CO_2 and H_2S	100 – 600 ppm H_2S, 33 – 35% CO_2	0.56 - 1.25 kg H_2S t^{-1} Ash 35 kg CO2 t^{-1} Ash and 135 kg CO_2 t^{-1} Ash.	50 for H_2S, not feasible for CO_2	NA	Not feasible for CO_2 removal, ashes could not be reused for as fertilizer.	Juárez *et al.* (2018)
T3, T4 soil substrates	H_2S	771 - 819 ppm	0.0048 m^3h^{-1}	93, 97	20.8, 20.1 g-S/100g	A constant flow rate <0.006 m^3/hr to prevent large pressure drop	This study
Moss substrate	CO_2, NH_3, H_2S	CO_2- 31.6%, H_2S – 307 ppm, NH_3 – 13 ppm	0.006 m^3h^{-1}	59 - CO_2,38 -NH_3 68-H_2S	1.8 g-S/100 g of sorbent	The flow rate <0.0048 m^3/hr to prevent intoxication of microbes by NH_3 and H_2S present	This study
Cryptogamic filter	CO_2, NH_3, H_2S	CO_2 – 38%, NH_3 – 8.7 ppm, H_2S - 819 ppm	0.006 m^3h^{-1}	99.7-CO_2, 77.2-NH_3, 98.6-H_2S	11 g-S/100 g	It does not work on high pressure, high flow rate operation and requires water scrubber for removal of excess Oxygen.	This study

Sethupathi *et al.* (2017) observed that the adsorption performance of a fixed bed column was significantly improved by the physical and chemical properties of biochar on CO_2 and H_2S removal. It also revealed that biochar has a relatively low effect on CH_4 adsorption. Therefore, CH_4 content is unaffected during the whole adsorption process. Juárez *et al.* (2018) in his study on biogas purification with biomass ash, found that the ash was successful in removing both CO_2 and H_2S, but to an extent, CO_2 removal was affected by high filter rates. This study has addressed the flow rate to ensure maximum gas reaction time to allow considerable adsorption of CO_2 by biochar and moss substrates. The presence of moisture by which cryptogams thrive provides a humid condition for further removal of CO_2 and H_2S gases. The filter has integrated the physical and chemical properties of these substrates to facilitate the removal of these impurities from the gas.

Other multiple gas removal filters were designed for the removal of more than one pollutant from the gas; results have shown significant removal for one gas but relatively poor for the other gases (Juárez *et al.*, 2018). The primary advantages of biological filters were low energy requirements, mild operations and regeneration capability of the materials (Kim *et al.*, 2004; Vannini *et al.*, 2008). The disadvantage of using these methods was the low flow rate required for operation, additional nutrients were required, clogging of the bed due to sulfur deposit and a small amount of O_2, N_2 and moisture was left in the treated biogas (Zhao *et al.*, 2010).

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Biofiltration system integrated with four types of soils, T1, T2, T3, or T4, with biochar and cryptogamic cover, was designed and tested on-site for removal biogas impurities in the form of CO_2, H_2S and NH_3. The function of each substrate was elaborated via a special experimental arrangement. Among the samples, the T3 and T4 soils demonstrated the best H_2S removal with sorption capacities of 20.8 and 20.1 g-S/100 g and RE of 93% and 97% respectively. This good performance of the soils attributed to their high iron content, large cation exchange concentration and organic carbon percentage. Moss and carbon-based material (biochar) showed inadequate H_2S removal, indicating that pure physical adsorption was not efficient on digesters operating at low pressures such as in typical farm. Moss substrate had significantly high CO_2 RE of 59% and as low as 38% for NH_3 during the 60 min of the experiment.

Integrating these substrates in a bed arrangement of a packed biofilter improved the overall adsorption of CO_2, NH_3 and H_2S. The most important advantage of a cryptogamic biofilter over other physical-chemical technologies is that, it is applicable in a wide range of pollutants (impurities), effective in low concentration, can be used under ambient conditions (pressure, temperature and pH), consumes very little energy, materials are easy to obtain, simple to operate and economic. Another advantage is flexibility, as they are quick to respond to the changing pollutant characteristics because of the wide range of microbial metabolic pathways.

5.2 Recommendations

The Combustion of biogas fuel that contains H_2S gas produces intoxicating fumes that are harmful to human health with respiratory ailments such as bronchitis and asthma. As discussed, the solution to this is, therefore, to remove these contaminants from the gas. This study recommends that the biofilter for the removal of biogas contaminants be built adjacent to the biodigesters to provide efficiency, the well-being of the consumers as well as the safety of the environment. The lab experiment on the biofilter performance is also of importance, but in this work, it was not done so far; only on-site tests were conducted. It is recommended to conduct the lab tests at steady conditions for further analysis of biogas impurities adsorption by biofilter components.

Further research on biofilters may help explain the influence of prolonged time and reliability of the filter towards improving it. Also, to enhance the performance of the filter the following tests can be suggested:

(i) Further tests to be performed on the site at controlled conditions over a long period to verify sustainability of the filter and contaminant removal rate.

(ii) The effect of moisture and humidity on the filter performance particularly on the settling of the bed materials, gas removal and how it affects the gas calorific value.

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APPENDICES

Appendix 1: The soil samples and Profile Statistics collected from Tanzania Agricultural Research Institute (TARI) located in Tanga

	Location	Sample	Depth	Physical Properties
 World Reference Base for Soil Resources WRB (FAO, 2014): Lixic Rhodic Ferralsol (Clayic, Cutanic, Profondic)	KGR P/5	A1	0-15/20 cm	Dark red 2.5 YR 3/6 dry, 2.5 YR 2.5/4 dark reddish brown moist; clay, slightly hard dry, friable moist and sticky
 World Reference Base for Soil Resources WRB (FAO, 2014): Endocalcaric Stagnic Luvisol (Eutric, Humic, Profondic)	KGR P/6	Ap	0-20/25 cm	Black 10 YR 2/1 moist; clay loam, friable moist, sticky and plastic wet; moderate fine and medium sub-angular blocks.
		Btg1	20/25-40 cm	Very dark greyish brown 10 YR 3/2 moist; clay, very firm moist, sticky and plastic wet;

	Location	Sample	Depth	Physical Properties
				moderate medium and coarse angular blocks;
 World Reference Base for Soil Resources WRB (FAO, 2014): Rhodic Lixisol (Clayic, Cutanic Profondic)	KGR P/6	Ap Btg1	0-20/25 cm 20/25-40 cm	Black 10 YR 2/1 moist; clay loam, friable moist, sticky and plastic wet; moderate fine and medium sub-angular blocks; many fine and very fine pores; common fine and very fine roots; Very dark greyish brown 10 YR 3/2 moist; clay, very firm moist, sticky and plastic wet; moderate medium and coarse angular blocks; patchy thin clay cutans; brown

Appendix 2: Mass composition of soil in the Filters

Soil type	Filter type	Weight of empty container (g)	Weight of aerator and small gravels	Weight of soil sample (g)	Weight of charcoal dust (g)	Weight of gravel packs (g)	Weight of moss substrate (g)	Total weight of the filter (g)
T1, T2, T3 and T4	1	100	200	100	100	1200	545	2245
	2	100	200	150	100	1200	545	2295
	3	100	200	100	100	1200	545	2345

Appendix 3: On site setup of the experiment