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Removal of hydrogen sulfide and ammonia from biogas using Oldoinyo Lengai Volcanic ash

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**REMOVAL OF HYDROGEN SULFIDE AND AMMONIA FROM
BIOGAS USING OLDOINYO LENGAI VOLCANIC ASH**

Isack Kandola

**A Dissertation Submitted in Partial Fulfilment of the Requirements for the Degree of
Master's of Science in Materials Science and Engineering of the Nelson Mandela
African Institution of Science and Technology**

Arusha, Tanzania

February, 2019

ABSTRACT

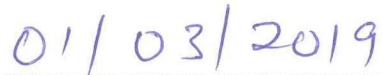
Oldoinyo Lengai mountain located in Northern Tanzania is the only active natrocarbonatite volcano with unusually alkali-rich natrocarbonatites which are not found elsewhere in the world. Volcanic ash formed earlier during eruptions was collected from different sites along the mountain, and its potency to adsorb hydrogen sulfide (H₂S) and ammonia (NH₃) from biogas was investigated. The samples were calcinated at different temperatures (550–850 °C) and were characterized by X-ray fluorescence, scanning electron microscopy and X-ray diffraction techniques. The on-site adsorption experiments were conducted at the biogas digester at ambient conditions. The calcinated ash was packed into the reactor bed, biogas allowed to pass through the adsorbent, and the inlet and outlet concentrations of H₂S and NH₃ were measured. The height of the site where the adsorbent was taken from, calcination temperature, biogas flowrate and mass of the adsorbent were variable parameters and found to influence greatly on the efficiency of H₂S and NH₃ removal. The efficiency increased with calcination temperature raise and mass of adsorbent and decreased with flowrate increase. The samples collected from the top site of the mountain and calcinated at 850 °C exhibited the best sorption performance (SC) of 1.0 g of S/100 g of adsorbent when the mass of adsorbent of 1 g and the biogas flowrate of 0.002 m³/min were used as standard parameters for this study. Chemisorption of H₂S was confirmed *via* bornite and hexahydrite, while CO₂, confirmed *via* trona, pirssonite and nahcolite while NH₃ was detected by gas analyzer.

DECLARATION

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



Isack Bernard Kandola

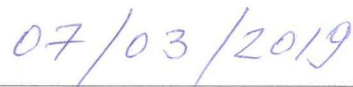


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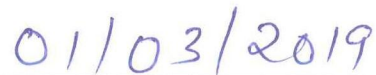
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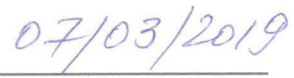
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CERTIFICATION

The undersigned certify that they have read the dissertation titled “**Removal of Hydrogen Sulfide and Ammonia from Biogas using Oldoinyo Lengai Volcanic Ash**” and recommended for examination in fulfillment of the requirements for the degree of Master’s of Science in Material Science and Engineering of the Nelson Mandela African Institution of Science and Technology.



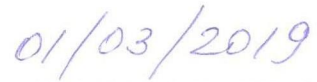
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Dr. Cecil Kithongo



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DEDICATION

Dedication to my lovely children and family members for always being supportive of my education. Their inspiration and prayers encouragement from them were highly appreciated.

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LIST OF ABBREVIATIONS AND SYMBOLS

OLA	Oldoinyo Lengai volcanic ash
XRF	X- ray fluorescence
XRD	X- ray diffraction
TP	White ashes without plants collected on top
TN	White ashes with plants
RT	Ambient temperature
MN	White ashes with plants collected at medium
MX	Mixture of black and white ashes
BN	White ashes with plants collected at bottom
ppm	Parts per million
SEM	Scanning electron microscopy
EDS	Energy dispersion spectroscopy
GHSV	Gas hourly space velocity
SC	Sulfur sorption capacity
R	Percentage removal
BT	Breakthrough time
C _{in}	Inlet concentration
C _{out}	Outlet concentration
M	Atomic mass of sulfur
T _c	Calcination temperature

CHAPTER ONE

INTRODUCTION

1.1 Background of the study

The removal of H₂S and NH₃ as toxic components from the biogas stream is an important environmental issue which many researchers focused on globally (Karmakar *et al.*, 2015). The hydrogen sulfide in biogas causes corrosion of metal components, such as regulators valves, gas meters, and mountings. Also, combustion of biogas containing H₂S produces poisonous sulfur dioxide (SO₂), which dissolves in engine oil causing the oil to become acidic and lose its ability to lubricate (Nicolas and Steve, 2009). Ammonia (NH₃) in biogas stream originates from degradation of biomass proteins (animal and other protein containing wastes used in bio digesters). When released free to the atmosphere, it endures a number of chemical reactions troubling the atmospheric equilibrium. In presence of acidic rain, NH₃ forms ammonium salts particles, which interfere with cloud formation and cloud particle circulation (Dämmgen and Erisman, 2005). It also contributes to the formation of NO₂ gas which is a greenhouse gas (Wulf *et al.*, 2002; Kirkby *et al.*, 2011). Furthermore, ammonia is a neurotoxin that causes irritation of mucous membranes, nausea and sudden death (Rao *et al.*, 2005).

Therefore, removal of H₂S and NH₃ from the biogas stream is very important for equipment protection and environmental conservation (Karmakar *et al.*, 2015). Many materials used for H₂S removal from biogas stream have been reported from different researchers (Nicolas and Steve, 2009). These are zinc oxide, iron oxide, biomass activated carbon, manganese oxide, copper oxide, potassium oxide, calcium carbonate oxide, municipal sewage sludge, soil containing metal oxides of nickel, chromium, lead, molybdenum, magnesium, cobalt, strontium, manganese, *etc.* (Siefers *et al.*, 2010). Studies have shown that oxide of iron and copper species are active components in reacting with H₂S from hot coal gas (Huang and Ko, 2015). Comparative test between copper and iron oxides indicated that iron oxides species were highly reactive and efficient in removing hydrogen sulfide from coal gas. The use of contaminated soil is a new technology which has a potential use in solving serious problems related to removing heavy metals and H₂S by applying into the method for hydrogen sulfide removal from coal gas stream at elevated temperature (Hsueh and Ko, 2012; Huang and Ko, 2015). Several technologies used to remove H₂S from biogas have been

reported such as the gas-gas membrane, alkaline/amine scrubbing, chemical oxidation, adsorption, bio-filtration, and catalytic wet oxidation (Lien *et al.*, 2014). Another method employed to remove H₂S is through H₂S oxidation using iron (Fe/MgO) catalyst at room temperature (Lien *et al.*, 2014). In addition, biological methods involve bacteria and fungi under anaerobic conditions consume H₂S to convert elemental sulfur to sulfur dioxide has been used (Sitthikhankaew *et al.*, 2014). However, all these materials and methods have disadvantages, such as huge investment costs, high operational cost and waste by-products disposal management matters (Awe *et al.*, 2017).

Furthermore, researchers have focused on developing methods of H₂S removal from biogas stream. These methods are mainly directed in fabrication of various materials to adsorb and capture H₂S from gas streams (Ho and Shih, 1992; Li *et al.*, 1997; Meeyoo *et al.*, 1997; Bagreev *et al.*, 2001; Kastner *et al.*, 2002; Ko and Chu, 2005; Nguyen-Thanh *et al.*, 2005; Ko *et al.*, 2006; Kim *et al.*, 2007; Seredych *et al.*, 2008; Sahu *et al.*, 2011; Mathieu *et al.*, 2013; Juárez *et al.*, 2017).

Currently, biogas sequestration through the adsorption process is a striking method due to its simplicity and low cost materials such as natural clay soils and red mud soils (Ko and Chu, 2005; Sahu *et al.*, 2011) rich in iron oxide; the latter being oxidizing agent to convert H₂S to elemental sulfur. Meanwhile, few studies have proposed the utilization of waste ashes (coal ash, biomass ash) (Ho and Shih, 1992; Kastner *et al.*, 2002; Vassilev *et al.*, 2010), kaolin and modified crude clay (Louhichi *et al.*, 2016), penausende muscovite (Sánchez-Martín *et al.*, 2008), laterite (Thanakunpaisit and Jantarachat, 2017), montmorillonite (Nguyen-Thanh *et al.*, 2005), which are economically feasible for carbon dioxide and H₂S removal.

The study aims at investigating the potential of Oldoinyo Lengai volcanic ash (OLA) in removing hydrogen sulfide from biogas plants at ambient temperature. The Oldoinyo Lengai is the only active natrocarbonatites volcano and it is unique source of alkaline ash in the world. The OLA is abundant and readily available; its composition has been critically characterized and analyzed (Rowe *et al.*, 1996; Carmody, 2012, Bremner and Banwart, 1976; Keller and Zaitsev, 2006; Zaitsev and Keller, 2006; Zaitsev *et al.*, 2008; Carmody *et al.*, 2013).

1.2 Statement of the Problem and justification of the study

Essentially, hydrogen sulfide is known to be toxic, corrosive gas that causes cancer, eye irritation and damage gas piping equipment (Nicolas and Steve, 2009). While ammonia causes upper airway irritation, lethal (causes death) within 5-10 min at 5 000 to 10 000 ppm exposure. Sustainable and safe use of biogas depends on the availability of technology or rather materials which would mobilize the toxic H₂S and NH₃ gas into less toxic, harmless or environmentally friendly substances. Ashes from different biomass sources and other several numbers of materials and methods have been used on removing H₂S and NH₃ as has been reported (Ko and Chu, 2005; Sahu *et al.*, 2011) (Ho and Shih, 1992; Kastner *et al.*, 2002; Vassilev *et al.*, 2010). The use of ashes appeared to be efficient in biogas stream cleanup and attractive because these materials are cheap and readily available which makes them promising in biogas purification.

Oldoinyo Lengai mountain volcanic ash contains compounds of K, Na, Ca, Zn, Fe, Mn *etc.* which are potentially effective in removal of hydrogen sulfide from biogas (Carmody, 2012). The materials were readily available, compared with other materials reported to be expensive, poisonous, tedious requiring much labor (Siefers *et al.*, 2010). To the moment, there were not enough measures to purify the biogas in Tanzania (Mwakaje, 2008; Torretta *et al.*, 2012; Laramee and Davis, 2013). In view of that, there was an urgent call to determine the performance of Oldoinyo Lengai volcanic ash materials that could be used to remove H₂S from biogas stream.

1.3 Objectives of the Study

1.3.1 General Objective

Evaluation of the performance of Oldoinyo Lengai volcanic ash in the hydrogen sulfide and ammonia removal from biogas.

1.3.2 Specific Objectives

- (i) Collection, preparation and characterization of samples.
- (ii) Measurements of H₂S and NH₃ removal.
- (iii) The evaluation of influence of height the samples were collected, calcination temperature, flowrate, and mass of adsorbent on the sorption capacity.

1.4 Research Questions

- (i) What is the chemical and mineralogical composition of the samples?
- (ii) What is the sorption capacitance of the samples for H₂S and NH₃ removal?
- (iii) What is the influence of height the samples were collected, calcination temperature, flowrate and mass of adsorbent on the sorption capacity?

1.5 Significance of the Study

The biogas production motivates most people especially those living in rural areas as an alternative energy source to electricity; it is readily locally available and environmentally friendly. Since the world is shifting towards renewable energy sources, biogas is among the renewable energy sources whose application gets increasing day to day; but there are fewer efforts and insufficient technology available for cleaning the gas coming from the biogas plants. Therefore, the rationale for the use of volcanic ash from Oldoinyo Lengai for removing H₂S from biogas will add more options to existing methods. Besides, this study is anticipated to add a solution for removing the health problems related to H₂S and NH₃ toxicity as well as prevention of corrosion from domestic and industrial equipment and reducing cost resulted from replacing equipment. In addition, the technology will promote development and better social life due to environmental conservation by reduction the amount of SO₂, SO₃ and NH₃ in the atmosphere which cause acid rains.

CHAPTER TWO

LITERATURE REVIEW

2.1 Materials for H₂S removal from biogas

Materials for H₂S removal from biogas are classified as; dry (solid) based materials, liquid-based materials, the methods used are; physical adsorption, chemical adsorption, and biological methods (Zicari, 2003; Kidnay *et al.*, 2011; Awe *et al.*, 2017). Zicari (2003) reported that dry basic materials involve solid metallic and alkaline materials such as iron oxide, hydrated lime; lesser materials were oxides of copper, zinc, lead, magnesium *etc.* These materials showed high efficiency for H₂S and NH₃ removal in various commercial application systems (Bandosz, 2002; Niesner *et al.*, 2013; Barelli *et al.*, 2017). Nevertheless, material availability and operational cost are the major drawbacks hindering successful utilization of the materials (McCollam, 2009). Besides, calcium aluminate supported by nickel oxide is also known for its ability to remove hydrogen sulfide from biogas stream at elevated temperature between 730 and 950 °C whereas, iron-rich soil and copper-rich soil materials are known for their effectiveness in remove hydrogen sulfide at the temperature ranging from 800 to 970 °C (Bagreev and Bandosz, 2005; Awe *et al.*, 2017). Iron oxide has been investigated for H₂S removal in different conditions at room temperature (Magomnang and Villanueva, 2014; Huang and Ko, 2015).

Furthermore, solutions of sodium, potassium carbonate (Lien *et al.*, 2014) have been reported to filter hydrogen sulfide from biogas stream by converting H₂S into elemental sulfur. The residual wastes disposal management is the major limitation for the process where the most waste are poisonous materials (Long and Loc, 2016).

Moreover, the impregnated carbon based materials include other zeolites, 13X, 5A, 4A, zinc and iron oxide nanoparticles which have an ability to remove H₂S in gas phase at ambient temperature, but most of these materials mainly rely on physical adsorption of a gas phase-particles onto a solid surface rather than chemical transformation which lower the removal efficiency and life of the adsorbent (Karmakar *et al.*, 2015). The main limitations are high cost, difficulties in preparation, and waste disposal management (Bagreev *et al.*, 2001).

On top of that the organic solvents such as, ethylene glycol, diethylene glycol *etc.*, are known to exhibit good performance in removing hydrogen sulfide from biogas stream

through the physical adsorption method, but the main limitation is formation of acid solution during the reaction which hinders their application and creating waste disposal management since they generate poisonous wastes (Zhao *et al.*, 2010).

Similarly, the biological materials which are based on bacteria like *Thiobacillus* phototrophic bacteria operates by capturing light energy and oxidize sulfide in the digester column (Tseng *et al.*, 2008). The major challenges behind these materials include: the need for repeated replacement of microorganism in the digester which is costly, tedious and hazardous. Also, difficulties in waste disposal management which require special procedures for treating wastes emanating from microorganisms and fluctuations of temperature that kills the microorganism in the digester source (Mahmood *et al.*, 2007; Awe *et al.*, 2017). Most of these materials are known as conventional adsorbents.

Therefore, Oldoinyo Lengai Volcanic ashes (OLA) is the new inorganic abundant natural materials which are accessible and relatively cheap to be used as adsorbent to remove H₂S and NH₃ in biogas stream.

2.2 Methods for H₂S removal

Methods used in removing of H₂S from biogas commonly are classified into three groups (Nicolas and Steve, 2009; Karmakar *et al.*, 2015). These groups include biotechnological methods, physical-chemical methods and the combination of biotechnological and physical-chemical methods.

2.2.1 Biotechnological methods

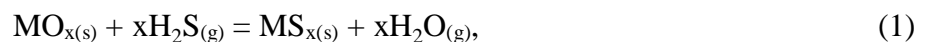
Biotechnological methods include the use of biotrickling filters, *etc.* (Rattanapan and Ounsaneha, 2011), to remove hydrogen sulfide from biogas through aerobic bacteria in bioreactors. Literature indicates that a variety of bacteria applied under anaerobic conditions have ability to oxidize hydrogen sulfide to elemental sulfur in the process called desulfurization (Syed *et al.*, 2006; Nicolas and Steve, 2009). Although the use of microbes has shown a big achievement for the biogas filtration but its main limitation is that, the bacteria are very sensitive to temperature in bioreactor which hinder the reaction process. Furthermore, there are other few more setbacks emanating from an application of microorganisms in the H₂S removal, include acidification of media due to sulfuric acid formation caused by degradation of the H₂S and sewage disposal management which raises

the operation cost and limits the application (Huang and Ko, 2015). Some bacteria, for instance, *Azospirillum* and *Thiobacillus* are capable for organic sulfur oxidizing, however, they active in liquid phase (Da Silva *et al.*, 2014).

2.2.2 Physical-chemical methods

Essentially, a physical method involves many methods such as activated carbon which contains pores with large internal surface (Sitthikhankaew *et al.*, 2014). These are prepared by incomplete combustion of raw materials like, coal, petroleum coke, polymers or materials like coconut shells, grain pine wood and bagasse (Baçaoui *et al.*, 2001; Choo *et al.*, 2013). The use of palm shell activated carbon (PSAC) prepared by steam activation showed good results on removal of H₂S from biogas at temperature above 30 °C while alkaline impregnated carbon was effective at high temperature to about 550 °C (Bagreev *et al.*, 2001). Despite its efficiency, physical methods use a strong base resulting in adsorbent wastes which in most cases are hazardous materials (Bagreev and Bandosz, 2005). In addition, the performance of activated carbon may be limited by moisture from biogas that tends to wet activated carbon surfaces and blocks its pores and lowers its efficiency and application of the technology (Sitthikhankaew *et al.*, 2011).

Awe *et al.* (2017) reported that physisorption methods involved the main uses of iron oxide, zinc oxide, magnesium oxide, an alkaline solution, and water scrubbing materials which showed good efficiency and mostly are traditionally still used as the simple methods for H₂S removal from biogas at high temperature. The general chemical reaction which describes this procedure is



where MO_x represents a metal oxide; MS_x represents metal sulfide (Hu *et al.*, 2012; Huang and Ko, 2015). The efficiency was limited by high operational costs in terms of materials availability (Nicolas and Steve, 2009).

The physical-chemical method opened new techniques of application of materials which used for hydrogen sulfide removal from hot coal gas by employing many soils containing important oxides such as; oxides of Fe, Cu, Zn, Mg, Ca, *etc.*, and to filter H₂S from biogas (Huang and Ko, 2015). Also, it has been reported that Fe₂O₃ from soil is essential candidate showed good efficiency in removing H₂S from biogas stream even at ambient temperature (Xia *et al.*, 2015; Louhichi *et al.*, 2016).

2.3 Performance of materials for removing H₂S from biogas stream

Generally, most materials used in chemical methods are non-cost effective, difficult in treatment but have been observed to have high-efficiency for H₂S removal from biogas stream at elevated temperature as has been reported in literature (Nicolas and Steve, 2009; Aita *et al.*, 2016). Iron oxide, zinc oxide, soil containing metal oxides and alkaline solids, have been applied as traditional adsorbents for many commercial industries related to H₂S removal from biogas (Novochinskii *et al.*, 2004).

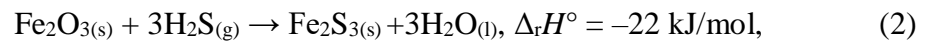
Iron oxide is the oldest material used to remove H₂S from biogas of about 99.9% efficiency by forming insoluble iron sulfide in the chemical products process and regenerated by allowing air to flow through bed-reactor to form iron oxide and elemental sulfur (Nicolas and Steve, 2009). The drawbacks have been reported (Bohn, 1989) that through the operation the fluidized bed reactor blocked with elemental sulfur and frequently needed to be substituted for new one which rises up the operation cost and disposal waste management (Nelson and Bohn, 2011).

Zinc oxide showed good efficiency for H₂S removal from biogas stream at elevated temperatures ranging between 200 and 400 °C (Lien *et al.*, 2014) through the use of fluidized bed reactor to react with zinc oxide to form an insoluble zinc sulfide (Kohl and Nielsen, 1997). Formation of irreversible zinc sulfide product lowered the efficiency of the material. Other materials of good efficiency to remove H₂S by chemical adsorption are alkali-earth metals such as hydrated lime Ca(OH)₂ which reacts with acid gases, H₂S, CO₂, through neutralization reaction in a fixed-bed reactor (Nicolas and Steve, 2009). Furthermore, many soils do exhibit a small chemical adsorption capacity for H₂S that is heavily dependent on the iron content (Bohn, 1989). Red soil contains naturally occurring iron oxides (Fe₂O₃, Fe₃O₄) and FeOOH which react with H₂S and CO₂ from hot coal gas to form elemental sulfur and water, through the packed fixed-bed reactor at an elevated temperature between 600 and 950 °C (Bohn, 1989; Nicolas and Steve, 2009). The removal process requires high temperature which is not cost effective (Huang and Ko, 2015).

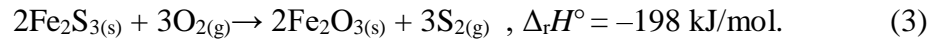
Soil materials contaminated with copper and iron have also been used for removing H₂S from hot coal gas which involves the reaction between metal oxides and H₂S (Hu *et al.*, 2012; Huang and Ko, 2015). Literally, the suitability of the performance of materials depends on availability of materials long life time and regeneration ability.

The basic redox equations at ambient temperature employed for adsorption and regeneration as given by (Bohn, 1989):

for purification process



for regeneration process



The OLA ashes fundamentally are in a group of natural materials which were investigated earlier in biogas sequestration, such as waste ashes (coal ash, biomass ash) (Ho and Shih, 1992; Kastner *et al.*, 2002; Vassilev *et al.*, 2010), kaolin and modified crude clay (Louhichi *et al.*, 2016), penausende muscovite (Sánchez-Martín *et al.*, 2008), laterite (Thanakunpaisit and Jantarachat, 2017), montmorillonite (Nguyen-Thanh *et al.*, 2005). OLA ashes are not only relatively cheap and effective materials but also environmentally friendly, nontoxic and can be applied as adsorbent which are economically feasible for H₂S removal from biogas stream at ambient temperature.

CHAPTER THREE

MATERIAL AND METHODS

3.1 Materials collection and preparation

Ashes used in this study were collected from Oldoinyo Lengai volcano which is located in Tanzania, the Rift Valley at 2°45' S, 35°55' E and 2000 m above the Serengeti plains (Hazen *et al.*, 2013; De Schutter *et al.*, 2015) as shown in Fig. 1.



Figure 1: Oldoinyo Lengai at Ngorongoro District in Arusha region (Mindat.org, 2016).

Several samples of ashes were randomly collected from various places on top, medium and bottom of the mountain. Previously it was found that the samples contain compounds of K, Na, Ca, Zn and Fe (Kastner *et al.*, 2002; Zaitsev and Keller, 2006; Carmody *et al.*, 2013; Juárez *et al.*, 2018) which are potentially effective for H₂S and NH₃ removal from biogas stream. The OLA samples were air dried, ground with a mortar and pestle, sieved to obtain the acquired particle size, below 2 mm, and stored in vacuum desiccators until used. The samples were calcinated at different temperatures T_c , 550 °C, 650 °C, 750 °C, and 850 °C for one hour in the oven (Thermo Scientific 1200 Box furnace) and then allowed to cool; the heating rate was 10 °C/min and cooling rate 20 °C/min. After the preliminary test on H₂S removal was performed, the best samples were retained for further investigations and detailed experiments. The selected samples were two from the top (OLA-TP and OLA-TN), two from medium (OLA-MN and OLA-MX) and one from bottom (OLA-BN), where TP and TN represent white ashes without and with plants, respectively; MN is white with plants and MX

is a mixture of black and white ashes with plants. The notation of the samples also includes the calcination temperature, e.g. OLA-TP-850 implies the sample was collected at the top site of the mountain and calcinated at 850 °C. The raw materials taken at room temperature (30 °C) are denoted as OLA-TP-RT.

3.2 Materials characterization

The oxides composition of the samples was determined by X-ray fluorescence spectrometer (XRF), model MiniPal 4 (Pw4030)-Rh manufactured by PANalytical, using software provided with the instrument. A sample of 25 g of calcinated adsorbent was added to 100 ml of distilled water. The mixture was stirred and shaken for one hour by using mechanical shaker (model AS 200, RETSH Company). The pH of samples was measured with a pH meter, model H199121. The moisture content of raw OLA ashes determined under standard procedures as has been reported elsewhere (Saka, 2012; Thanakunpaisit and Jantarachat, 2017) was found to be $22.2 \pm 0.5\%$. Mineral phase analysis and elemental oxide composition were analyzed by X-ray diffraction (XRD) technique using D2 phaser-Bruker model and X-ray diffraction meter with a Cu-K α radiation source in a 2θ range between 10° and 80° at a scanning rate of 2° min^{-1} and analyzed using EVA software provided with the instrument. In addition the sample were prepared according to the standardized PANalytical backloading system, which provides nearly random distribution of the particles.

The samples were analyzed using a PANalytical Aeris powder diffractometer with a PIXcel detector and phases were identified using X'Pert Highscore plus software. The relative phase amount (weight%) were estimated using the Rietveld method (Autoguan Program) as shown in Appendix 1 and 2.

The surface micromorphology of samples was investigated using a scanning electron microscope (SEM), model JEOL JSM-6335F with resolution of 500 nm, at 200 kV at the Department of Materials Science and Engineering, University of Connecticut, USA as shown in Appendix 3 and 4.

3.3 Measurements of H₂S and NH₃ removal and evaluation of sorption capacity of absorbents

The sorption experiment of H₂S and NH₃ was carried out at the Banana Investments company Ltd in Arusha, Tanzania where the biogas was produced from winery effluent banana

industrial waste. The biogas was liberated from upflow anaerobic sludge blanket between 100 and 120 m³ daily, the composition of the gas was determined with the biogas 5000 gas analyzer to be 82%–89% CH₄, 12%–15% CO₂, <1% O₂, 5-48 ppm of NH₃, and 24-60 ppm of H₂S (Makauki *et al.*, 2017).

A reactor made of plastic tube, 6.5 cm length, 1.7 cm diameter, filled with adsorbent supported by cotton wool on both end sides of the reactor tube. The biogas allowed to flow through the reactor at ambient temperature varying the flowrate from 0.0004 to 0.008 m³/min, and mass of adsorbents from 0.5 to 2.0 g. The mass of adsorbent of 1 g and the biogas flowrate of 0.002 m³/min were used as standard parameters for this study. Schematic diagram and photos of the experimental setup are shown in Figures 2 and 3. The flowrate was controlled and monitored by using a flow meter, model JBD2.5-SA. The concentration of H₂S and NH₃ was recorded at the inlet and outlet of the reactor with different time intervals from 5 to 150 min. Breakthrough time (*BT*) was noted when the outlet concentration C_{out} of H₂S and NH₃ reached 50% of the inlet concentration C_{in} . The sorption tests were repeated at least twice for each sample.

The performance of material adsorbent was specified as percentage removal R :

$$R = \frac{C_{in} - C_{out}}{C_{in}} \times 100 \quad (4)$$

Sulfur sorption capacity (SC) of the OLA samples, in grams of sulfur per 100 grams of sorbent, was determined as described in (Kim *et al.*, 2007; Tseng *et al.*, 2008; Garces *et al.*, 2012);

$$SC = GHSV \times \left[\frac{M}{V_{mol}} \times \int_0^t (C_{in} - C_{out}) dt \right], \quad (5)$$

where $GHSV$ is the gas hourly space velocity which is the volume of the gas flowing hourly through the reactor with 1 g of adsorbent (L h⁻¹g⁻¹); V_{mol} is the molar volume of the gas (L mol⁻¹) under standard conditions, M is the atomic mass of sulfur; C_{in} and C_{out} are the H₂S concentrations before and after sorption (ppm); t is the breakthrough time in hours.



Figure 2: Photos of the sorption experimental setup.

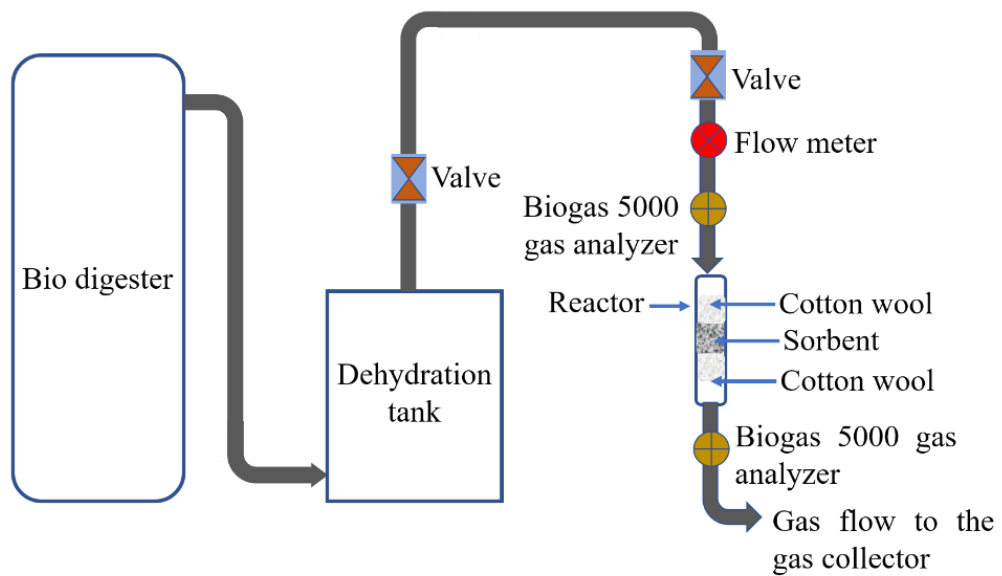


Figure 3: Schematic diagram of the sorption experimental setup.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 XRF analysis and pH of raw OLA samples

Results on the XRF analysis of the raw OLA samples (Table 1) show that Fe₂O₃, CaO and SiO₂ are most abundant components of all samples; alkali metal oxides are in essential amount, K₂O ~3%–10% and Na₂O ~2%–5%. Some of transition and rare-earth elements were also found. As is seen the content of these oxides changes with height the samples were collected. The composition of the OLA samples is rather promising for H₂S removal due to, as it was observed earlier (Kastner *et al.*, 2002; Seredych *et al.*, 2008; Juárez *et al.*, 2017), Fe, K, Ca, Zn, Na, Ti, and Sr oxides may act as catalysts for oxidation of H₂S.

Table 1: The composition (wt%) and pH values of Oldoinyo Lengai volcanic ash samples

Oxides	OLA-TP	OLA-TN	OLA-MN	OLA-MX	OLA-BN
Fe ₂ O ₃	25.40	24.60	24.40	24.60	21.10
K ₂ O	5.40	2.80	9.71	2.82	4.29
CaO	46.00	46.00	36.80	36.50	36.00
ZnO	0.20	0.13	0.20	0.10	0.10
Al ₂ O ₃	5.60	1.30			1.90
SiO ₂	5.10	11.00	19.40	21.20	24.00
TiO ₂	2.40	2.50	2.78	2.62	2.99
BaO	1.30	2.00	1.00	1.80	1.30
Na ₂ O	5.10	3.90	2.40	3.10	5.30
SrO	2.80	2.27	2.25	3.08	2.02
Eu ₂ O ₃	0.39	0.39	0.27	0.38	0.58
Nb ₂ O ₅	0.27	0.24	0.40	0.25	0.20
MoO ₃	0.04		0.07		
Total	100	97.13	99.68	96.45	99.78
pH	12.31	11.04	10.91	11.01	11.06

The pH values of the OLA ashes are in the range of about 11-12 and indicate materials' alkalinity which is evidently caused, according to (Zaitsev and Keller, 2006), by presence of iron, calcium, potassium and sodium compounds. The basicity of the OLA ashes is expected to favour the hydrogen sulfide removal as it was shown for example in (Seredych *et al.*, 2008). The mixed metal fly ashes (Ho and Shih, 1992; Kastner *et al.*, 2002; Seredych *et al.*, 2008), different metal oxides (Li *et al.*, 1997; Kastner *et al.*, 2002; Nguyen-Thanh *et al.*, 2005; Sánchez-Martín *et al.*, 2008; Sitthikhankaew *et al.*, 2011; Juárez *et al.*, 2017), coal ashes (Kastner *et al.*, 2002; Kastner *et al.*, 2003) were successfully used for H₂S removal from biogas stream at ambient temperature.

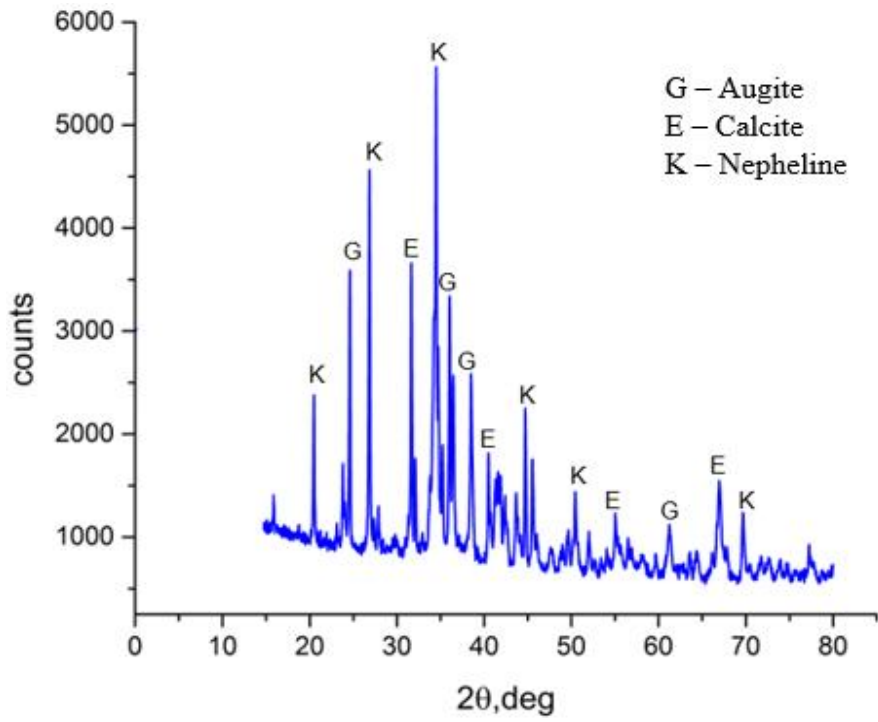
The mechanism of the H₂S adsorption/oxidation processes was considered in (Adib *et al.*, 1999; Ansari *et al.*, 2005; Bagreev and Bandosz, 2005; Cheng and Liu, 2007); it was shown that inorganic materials containing active metal oxides participate in this process. The H₂S was oxidized to sulfur due to presence of moisture, which enabled dissociation of H₂S into HS⁻ and then to elemental sulfur. These reactions were enhanced by basic pH of the adsorbent (Li *et al.*, 1997; Adib *et al.*, 1999).

4.2 XRD analysis of calcinated OLA samples

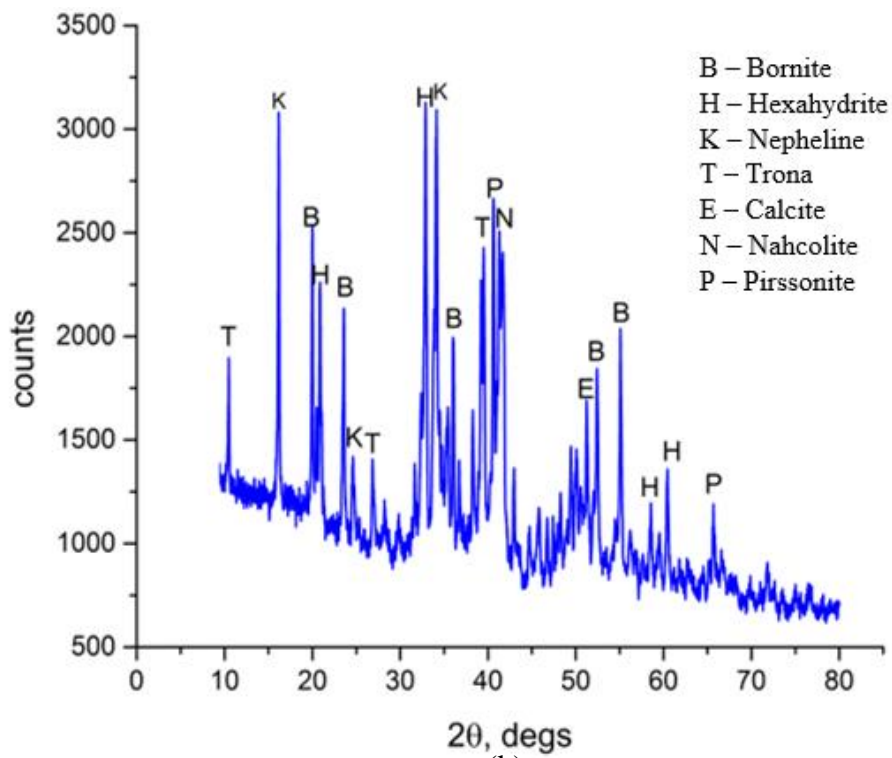
The XRD spectra were measured for several samples; an example for the OLA-TP-850 is shown in Figure 4(a) the data indicate the crystalline solid form of the materials by the peaks of augite Ca(MgAl)(Si₂Al)₆ has ($2\theta = 22^\circ, 35^\circ, 38^\circ$), calcite (CaCO₃) has ($2\theta = 30^\circ, 42.5^\circ, 54.5^\circ, 68^\circ$), nepheline (KNa₃Al₄SiO₁₆) has ($2\theta = 26^\circ, 35^\circ, 44^\circ, 49.9^\circ, 69.9^\circ$) before adsorption. These results are in accordance with the data reported previously (Zaitsev and Keller, 2006). For the sample after absorption, the additional peaks were recorded in Figure 4(b); hexahydrate (MgSO₄·6(H₂O)) has ($2\theta = 20^\circ, 34.1^\circ, 58.9^\circ, 59.9^\circ$), bornite (Cu₅FeS₄) has ($2\theta = 23^\circ, 25.2^\circ, 34.2^\circ, 55^\circ, 56^\circ$) which correspond to the adsorption of H₂S.

While trona, Na₃H(CO₃)₂(H₂O)₂, has ($2\theta = 10.1^\circ, 26^\circ, 37.9^\circ$), pirssonite CaNa₂(CO₃)₂(H₂O)₂, has ($2\theta = 38.1^\circ, 64^\circ$) and nahcolite, NaHCO₃, has ($2\theta = 40.5^\circ$) correspond to the adsorption of CO₂, while NH₃ concentration was not seen in the 5000-biogas analyzer after adsorption during measurement at time ranged from 0 to 20 min which implies that NH₃ was completely adsorbed. The NH₃ compounds were not seen through in XRD patterns probably due to low inlet concentration of ammonia, ranged from 0 to 0.005 mg per 1 g of the biogas. The formation of these compounds indicates interaction of hydrogen sulfide, carbon dioxide, and ammonia with the adsorbent and hence chemisorption occurrence. My results differ from those published (Sahu *et al.*, 2011) in which red mud was used for H₂S removal, and after sorption iron sulfide, pyrite, calcium sulfate, sulfur, sodium sulfide and bisulfide were formed.

Apparently, the distinction of our results with literature (Sahu *et al.*, 2011) may be attributed to the different mineralogical and chemical composition of the adsorbents.



(a)



(b)

Figure 4: XRD patterns for OLA-TP-850 sample (a) before and (b) after adsorption.

4.3. SEM surface micromorphology analysis

The surface morphology of the samples was investigated using SEM; an example shown in Figures 5(a) before and 5(b) after adsorption for OLA-TP-850. After adsorption the surface features showed crystalline white spherical particles that indicates considerable porosity which evidently provide efficient physisorption.

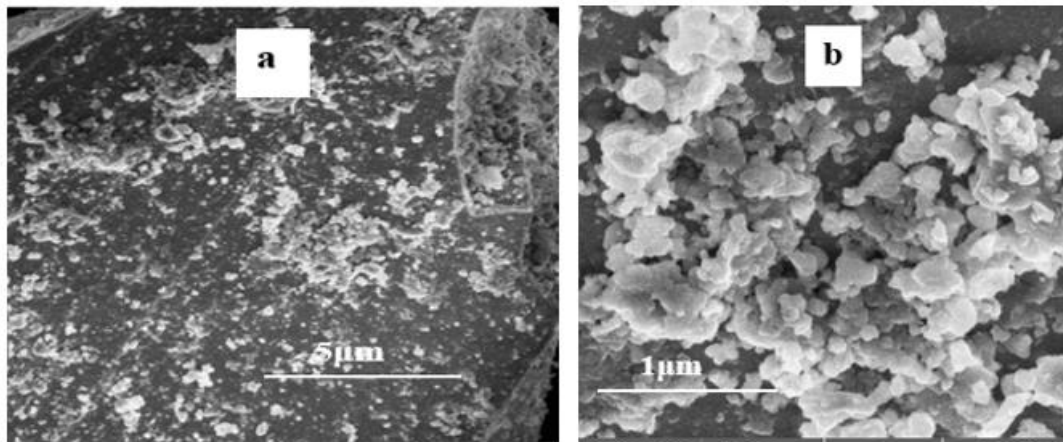


Figure 5: Surface morphology of OLA-TP-850 sample (a) before and (b) after adsorption.

It was observed earlier that the porous structure and surface chemistry of the adsorbent had significant effect on adsorption and oxidation of hydrogen sulfide (Nguyen-Thanh *et al.*, 2005). Besides the morphology of ashes is controlled by calcination temperature, and porosity increases with T_c increase (Ansari *et al.*, 2005). It may be expected that the samples which were calcinated at higher temperatures would demonstrate better adsorption performance.

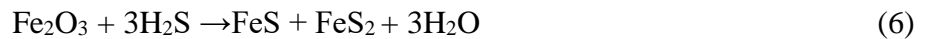
4.4 Adsorption performance of OLA samples

4.4.1. Effect of calcination temperature and height the samples were collected

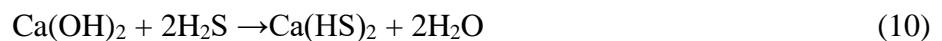
The values of sorption capacity calculated using Eq. (2) and breakthrough time are given in Table 2 for different OLAs. The effect of calcination temperature and height of sites the samples were collected on the sorption capacity is depicted also in the diagram (Figure 6). As is seen, the SC is increased with calcination temperature raise; e.g., the ashes taken without calcinations, OLA-TP-RT, and calcinated at 850 °C, OLA-TP-850, result in the SC of ~ 0.2 and ~ 1.0 g S/100 g of adsorbent, respectively. It is also observed that the SC increases with height of site; the samples collected at the top and calcinated at 850 °C, OLA-TP-850, demonstrate the best performance. The breakthrough time relates to the life time of the

adsorbent; the longer is the *BT*, the higher is the working capability of the material. One can see the *BT* increases greatly with height (from 5 min for OLA-BN-650 to 120 min for OLA-TN-650) and calcination temperature raise (from 55 min for the OLA-TP-RT up to 177 min for OLA-TP-850). Thus, the OLA-TP-850 samples possess the longest working time.

From the XRD results and results published elsewhere (Chiang *et al.*, 2000; Bagreev and Bandosz, 2005) about the mechanism of adsorption/oxidation that inorganic materials containing active metal oxides enhanced adsorption and oxidation of H₂S from gas phase. The H₂S oxidized to sulfur due to presence of moisture, which enable dissociation of H₂S into HS⁻ to elemental sulfur, contributed by basic pH adsorbent has been reported on coal based activated carbon modified by nitrogen (Ghosh and Tollefson, 1986; Bagreev *et al.*, 2004). Thus, the possible (6) to (14) reaction equations are as follows (Bagreev and Bandosz, 2005, Chiang *et al.*, 2000);



In addition, calcium or potassium hydroxide oxidizes H₂S to elemental sulfur as follows;



Furthermore, common reaction involved the reaction oxidation of H₂S to sulfur by presence of oxygen has been reported elsewhere (Meeyoo *et al.*, 1997) Thus, the adsorption reaction may be written as follows;



Table 2: Adsorption performance of different OLA samples for H₂S removal: sorption capacity and breakthrough time; mass of adsorbent 1 g and the biogas flowrate 0.002 m³/min.

Sample	SC, g of S/100 g of adsorbent	BT, min
OLA-TP-RT	0.24	55
OLA-TN-RT	0.21	35
OLA-MN-RT	0.08	20
OLA-TP-550	0.65	120
OLA-TN-550	0.37	80
OLA-MN-550	0.17	35
OLA-MX-550	0.05	10
OLA-TP-650	0.82	150
OLA-TN-650	0.53	120
OLA-MN-650	0.35	80
OLA-MX-650	0.16	35
OLA-BN-650	0.02	5
OLA-TP-750	0.90	165
OLA-TN-750	0.58	150
OLA-MN-750	0.47	120
OLA-MX-750	0.18	35
OLA-BN-750	0.03	5
OLA-TP-850	1.00	177
OLA-TN-850	0.67	150
OLA-MN-850	0.59	120
OLA-MX-850	0.25	55
OLA-BN-850	0.04	10

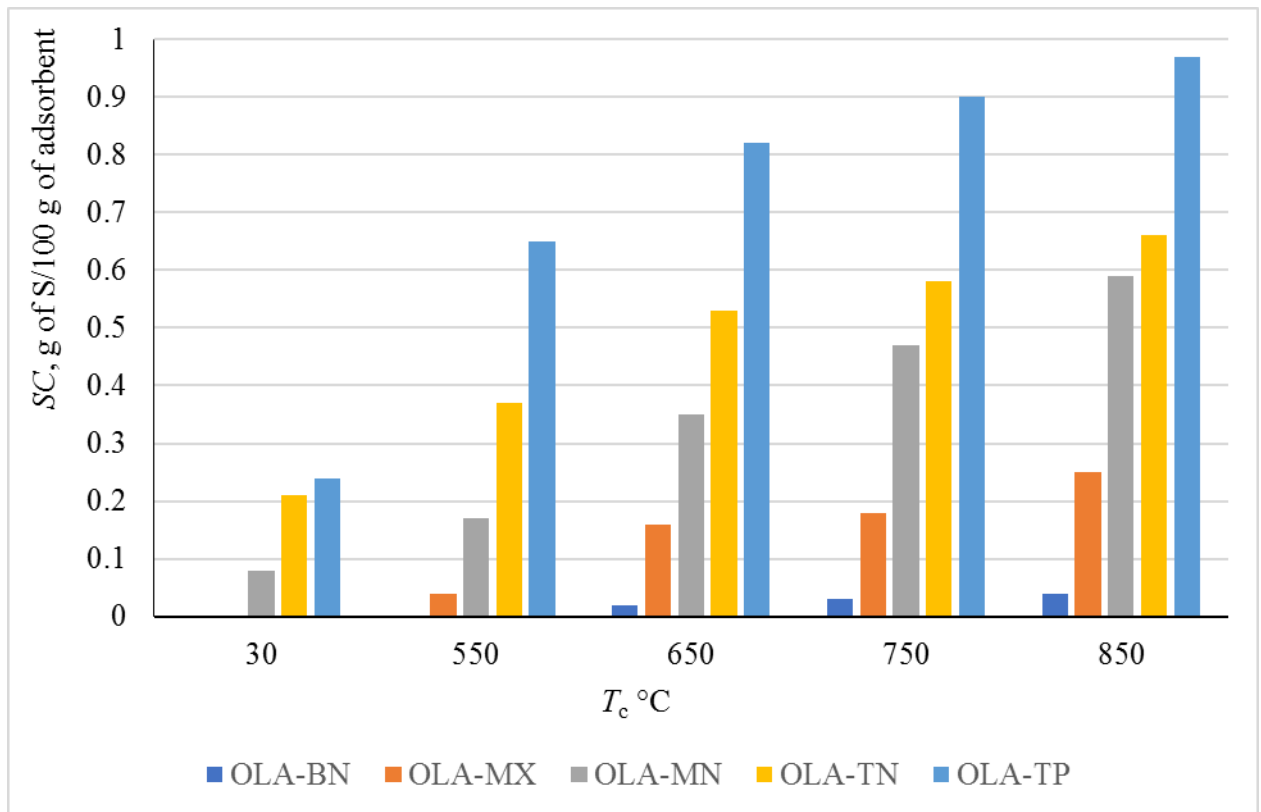


Figure 6: Sorption capacity of Oldoinyo Lengai ash materials for hydrogen sulfide removal.

The adsorption efficiency removal R was measured both for H_2S and NH_3 and analyzed for different samples with respect to time interval between the measurements of initial and final concentrations of the adsorbates while biogas flowed through the reactor. The plots for R vs time for the samples collected at different heights and calcinated at 850 °C are shown in Figure 7. Results indicate the removal efficiency decreases with time for all samples. For the OLA-TP-850, R reduces by ~10% both for H_2S and NH_3 after one hour of the adsorbent use.

Similar trend is observed in Figure 8 where the plots of R vs time are given for OLA-TP samples calcinated at different temperatures. The removal efficiency is increased with calcination temperature raise. Thus after 150 min of the adsorbent use, the R of OLA-TP-RT descends to 37%, while the OLA-TP-850 holds 60% for H_2S removal; for ammonia, the values of R are 40% and 80%, respectively. Based on the results of (Nguyen-Thanh *et al.*, 2005; Itodo *et al.*, 2010; Mathieu *et al.*, 2013), we suggest that the increase in adsorption efficiency with temperature T_c may be caused by increase of number of pores created in adsorbents. On the other hand, the removal efficiency decreases in time because the surface of adsorbent is being occupied with the adsorbate molecules and the porosity is reduced as the pores are clogging with the gas molecules (Thanakunpaisit and Jantarachat, 2017).

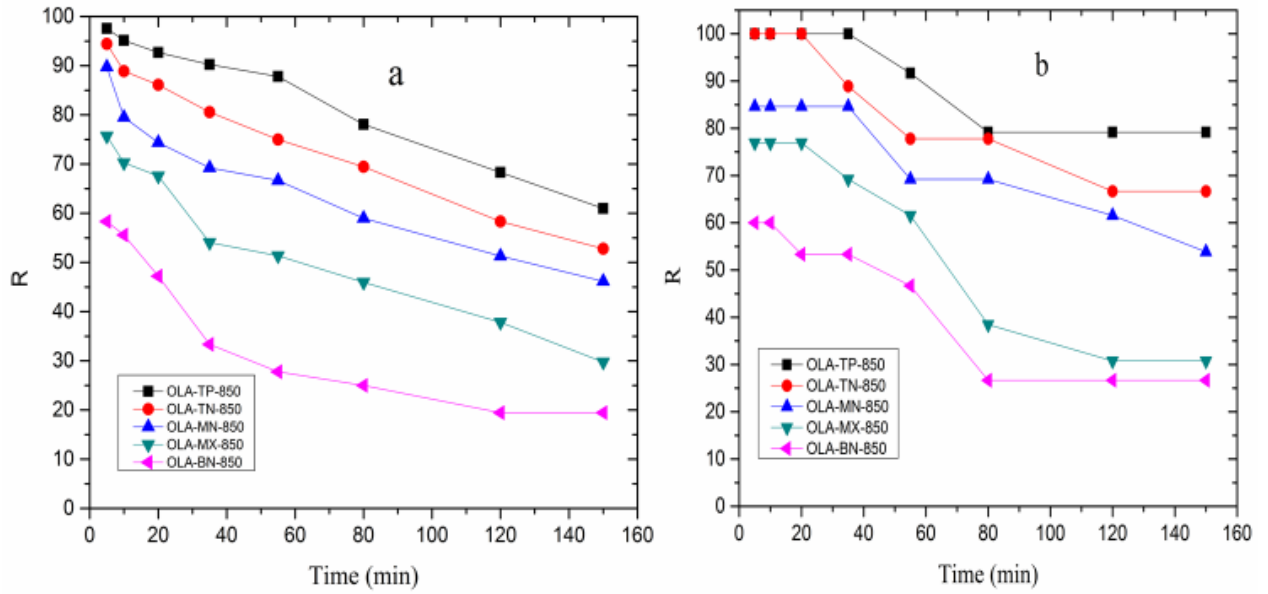


Figure 7: Effect of the site location on the removal efficiency of H_2S (a) and NH_3 (b); for all samples $T_c = 850$ °C, flowrate 0.002 m^3/min , mass of the adsorbent 1 g.

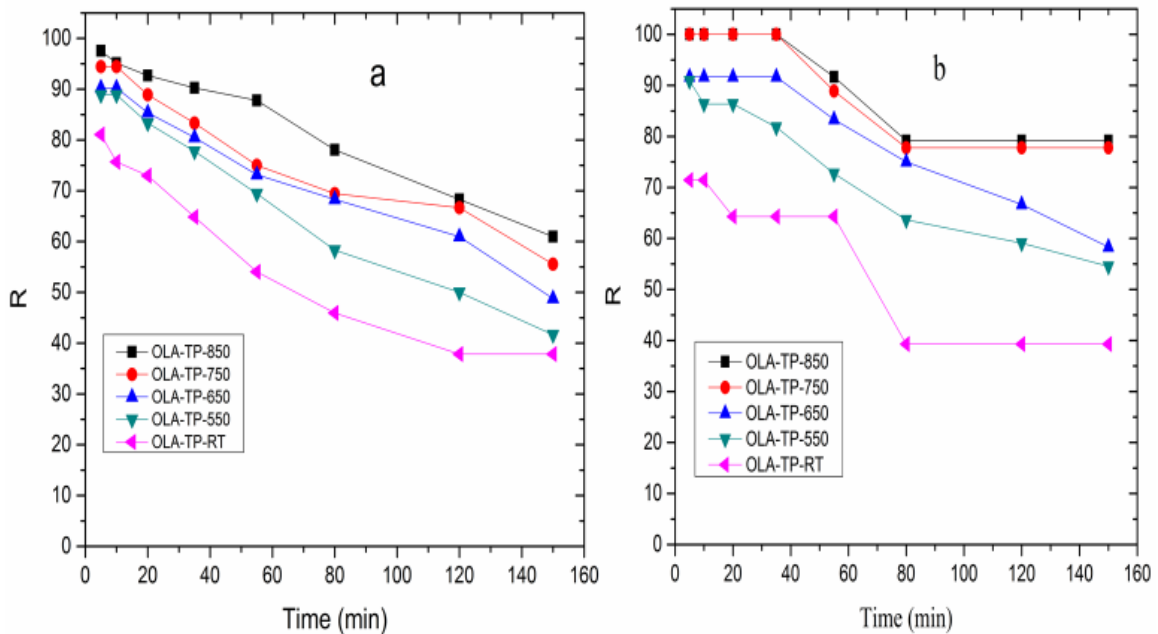


Figure 8: Effect of calcination temperature on removal efficiency of H_2S (a) and NH_3 (b); OLA-TP samples, flowrate 0.002 m^3/min , mass of the adsorbent 1 g.

If compare the plots of R vs time for H_2S and NH_3 , they look differently: monotonic decay for the former and step-like for latter. The step-like behavior for ammonia may be attributed to rather low concentration ($C_{in} \sim 0.005$ mg NH_3 per 1 g of the biogas, that is one order less than of H_2S) measured at the sensitivity limit of the gas analyzers. Moreover, according to Eq. (4), the lower input concentration of ammonia also brings bigger value of R .

Therefore, among all OLA samples considered the ashes collected at the top site and calcinated at 850 °C, the OLA-TP-850, demonstrated the best removal efficiency retaining it high during the exploitation time of the adsorbent.

4.4.2. Effect of biogas flowrate

The effect of biogas flowrate on the samples adsorption performance was investigated; the flowrates were 0.0004, 0.001, 0.002, and 0.008 m³/min. The values of the removal efficiency of H₂S and NH₃ are plotted vs time for the top-site samples OLA-TP-850 in Figure 9. One can see, with the flowrate raise from 0.0004 to 0.008 m³/min the *R* values decrease from 71% to 20% for H₂S and from 100% to 58% for NH₃, respectively, measured after 150 min adsorbent's use.

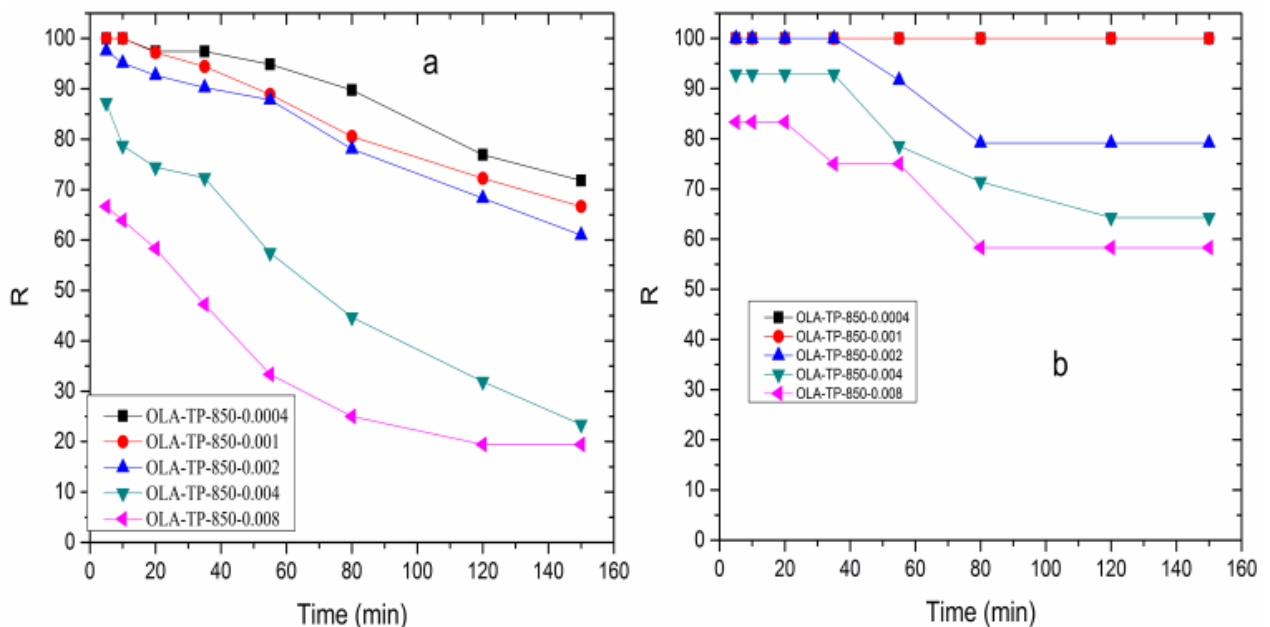


Figure 9: Effect of biogas flowrate on removal efficiency of H₂S (a) and NH₃ (b); OLA-TP-850, mass of the adsorbent 1 g.

It seems at low flowrate (0.0004 m³/min) the materials get enough contact time for interaction between gas molecules and adsorbent; whereas at high flowrate (0.008 m³/min), H₂S and NH₃ gas molecules can pass through without being adsorbed and reacted fully with adsorbent. Therefore, the contact time between gas and adsorbent is significant in determining the adsorption capacity. This is in accordance with findings reported in (Li *et al.*, 1997).

4.4.3. Effect of mass of adsorbent material

The effect of variation of the adsorbent mass, from 0.5 to 2.0 g, on the removal efficiency of H_2S and NH_3 ; was considered for the samples OLA-TP-850 (Figure 10). The results indicate that R values evidently increase with mass. Four-fold enlargement in mass leads to essential increase in removal efficiency, from 23 to 80% for H_2S and from 50% to 100% for NH_3 measured after 150 min adsorbent's use. When the mass of adsorbent was 2 g, the material retained 100% H_2S removal after 40 min and efficiency decreased to 80% after 150 min; while for NH_3 the adsorbent held 100% removal efficiency for all time measurements.

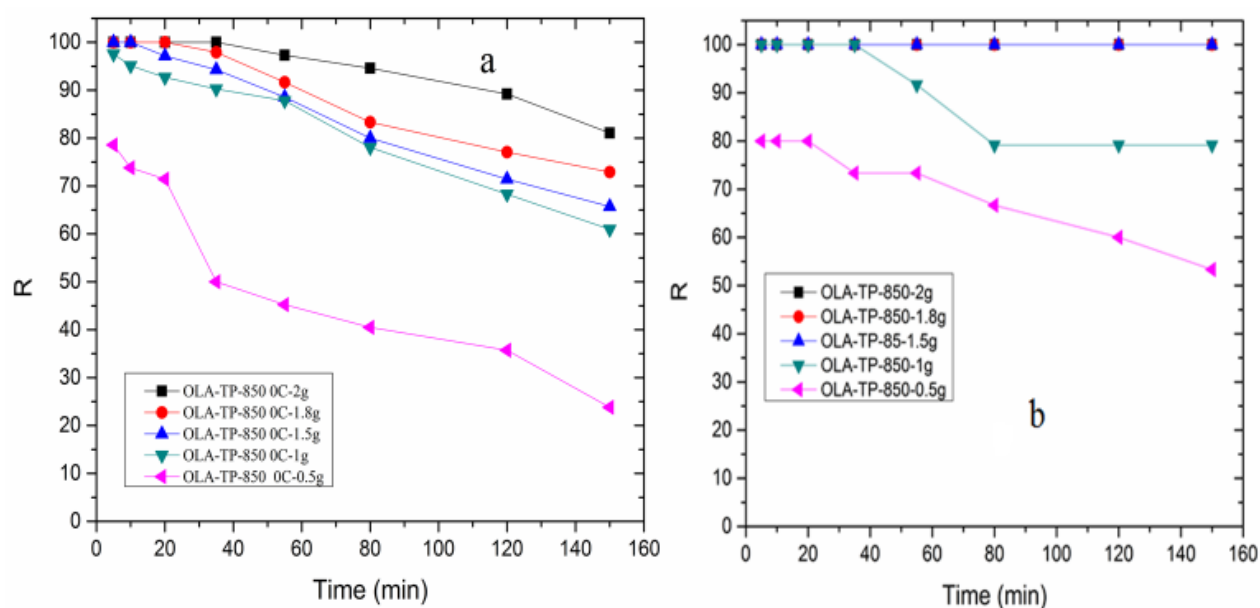


Figure 10: Effect of biogas flowrate on removal efficiency of H_2S (a) and NH_3 (b); OLA-TP-850, mass of the adsorbent 1 g.

4.4.4. Comparison of OLA-TP-850 with other materials

The adsorption properties of our best sample OLA-TP-850 are compared to other materials reported in literature (Table 3).

Table 3: Adsorption properties of OLA-TP-850 compared to other materials.

Adsorbent	Mass, g	Biogas flowrate, m ³ /min	H ₂ S removal, g S/100 g of adsorbent	pH	Ref.
Moist soils	1–5	8.00×10 ⁻⁵	0.50	5.70–7.70	(Bremner and Banwart, 1976)
Montmorillonite clay	12.50	51.00×10 ⁻²	1.27	9.00	(Nguyen-Thanh <i>et al.</i> , 2005)
Municipal waste bottom ash	13×10 ³	55.94×10 ⁻³	0.30	9.80	(Ducom <i>et al.</i> , 2009)
Red mud soil	5	5×10 ⁻⁵	2.10	> 13.00	(Sahu <i>et al.</i> , 2011)
Coal ashes	10	14.20×10 ⁻⁵	0.50	11.90 ± 0.01	(Kastner <i>et al.</i> , 2002)
OLA-TP-850	1	2×10 ⁻³	1.00	12.31	Current study

The sorption capacity of OLA ashes appeared to be close to the commercial montmorillonite clay and higher than other natural materials used for H₂S removal, e.g. municipal waste bottom ash, coal ashes *etc.* Meanwhile, when different samples are compared it is worth to take into account the effect of experimental conditions like the biogas flowrate and pH; as it was mentioned above, the lower flowrate and basicity of the sorbent favour the hydrogen sulfide removal. Thus, the Oldoinyo Lengai volcanic ashes can be used as adsorbents for H₂S and NH₃ removal in biogas plant industries, however further improvement of the adsorption properties may be suggested, e.g., increasing of calcination temperature and activation with chemical reagents.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this dissertation, biogas filtration using Oldoinyo Lengai ashes has been studied. The main objective was to evaluate the Oldoinyo Lengai volcanic ash performance for the hydrogen sulfide and ammonia removal from biogas stream. To achieve this, the specific objectives were collection, preparation and characterization of samples, measurements of H₂S and NH₃ removal, and evaluation of the height the samples were collected, calcination temperature, flowrate, and mass of adsorbent on t

he sorption capacity. The study was guided by the questions as follows. What is the chemical and mineralogical composition of the samples? What is the sorption capacitance of the samples for H₂S and NH₃ removal? What is the influence of height the samples were collected, calcination temperature, flowrate, and mass of adsorbent on the sorption capacity?

The physical characteristics such as surface morphology and crystal pattern of the samples were studied; efficiencies of adsorption and sorption capacity of the materials also were examined. Sorption capacity and removal efficiency were measured for different OLA samples at ambient temperature. The materials were examined in the on-site experiment at real industrial conditions. The best materials demonstrated long-lasting sorption ability. The XRD, SEM and XRF spectra of the OLA samples, were examined. Mineralogical composition analysis exhibited an abundance of compounds of iron, alkali and alkali-earth metals; rare-earth metals compounds were also found. The high porosity of samples favoured physisorption of H₂S and NH₃. Moreover, chemisorption of H₂S was confirmed via bornite (Cu₅FeS₄) and hexahydrite (MgSO₄·6(H₂O)) formation after sorption, while CO₂ and NH₃ removal was confirmed via trona Na₃H(CO₃)₂(H₂O)₂, pirssonite CaNa₂(CO₃)₂(H₂O)₂ and nahcolite NaHCO₃ formation.

5.2 Recommendations

In my on-site experiment, the biogas flowrate and mass of adsorbent were variable parameters. The inlet concentration of H₂S in biogas was controlled but difficult to keep constant. For the next step of investigations, the recommendations are as follows;

- (i) Evaluate the effect of concentration of H₂S and NH₃ on the sorption capacity of the samples in laboratory conditions that will allow keeping constant the inlet concentrations.
- (ii) The adsorbents investigated should be developed to commercial level to reach the beneficiaries and biogas stakeholder's demands.
- (iii) The ashes are powdery in nature which hinders the gas flow; therefore, the materials should be incorporated in form of pellets to maintain the gas flow rate.
- (iv) To study regeneration of the materials.
- (v) To use GPS navigation device during sample collection in order to investigate the effects and relationship between performance and site location of the mountain.
- (vi) To use BET, FT-IR, TG analysis and SEM with the same magnification for materials before and after adsorption for better characterization.

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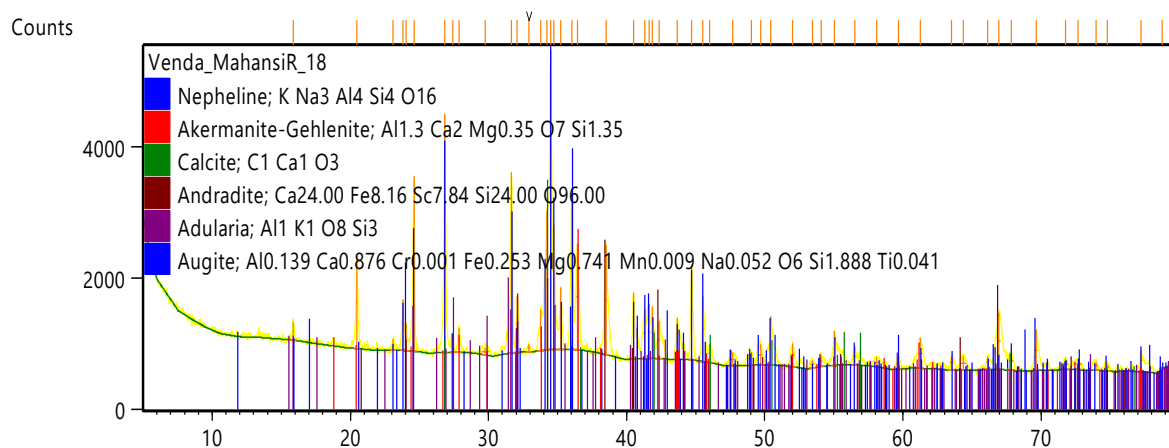
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APPENDICES

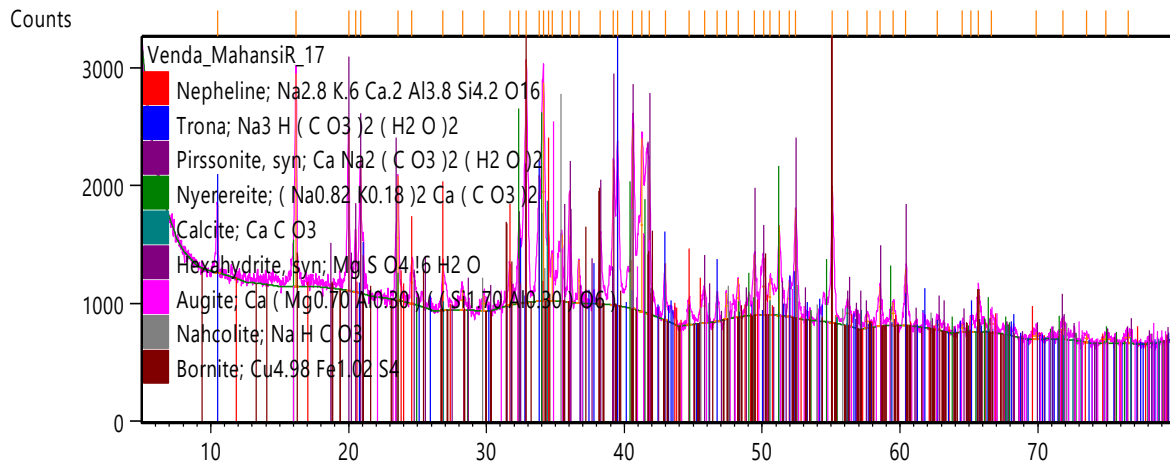
The analysis were performed at The University of Venda, Pretoria 002, South Africa.

Appendix 1: XRD patterns and mineral compositions for OLA-TP-850 sample before adsorption.



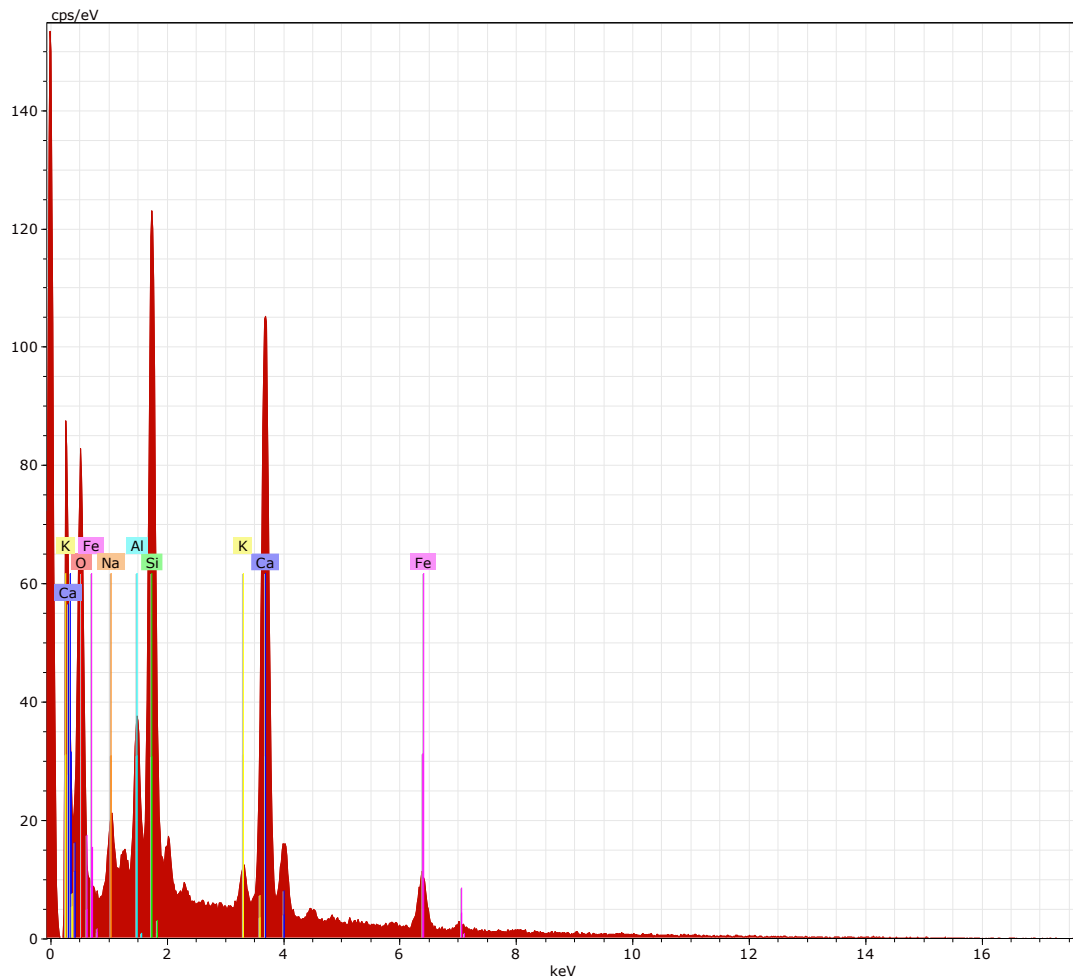
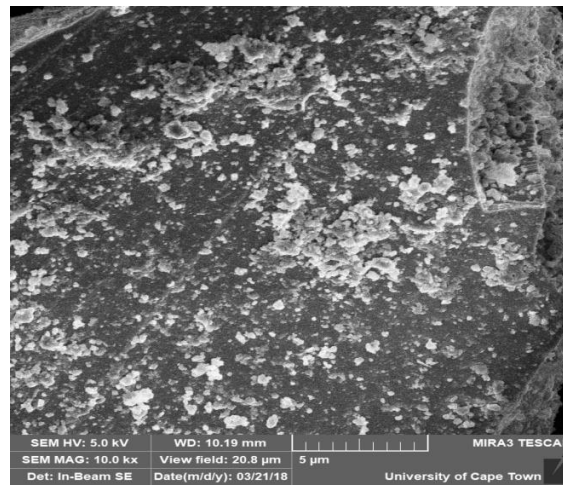
Peak List
Nepheline; K Na ₃ Al ₄ Si ₄ O ₁₆
Akermanite-Gehlenite; Al _{1.3} Ca ₂ Mg _{0.35} O ₇ Si _{1.35}
Calcite; C ₁ Ca ₁ O ₃
Andradite; Ca _{24.00} Fe _{8.16} Sc _{7.84} Si _{24.00} O _{96.00}
Adularia; Al ₁ K ₁ O ₈ Si ₃
Augite; Al _{0.139} Ca _{0.876} Cr _{0.001} Fe _{0.253} Mg _{0.741} Mn _{0.009} Na _{0.052} O ₆ Si _{1.888} Ti _{0.041}

Appendix 2: XRD patterns and mineral compositions for OLA-TP-850 sample after adsorption.

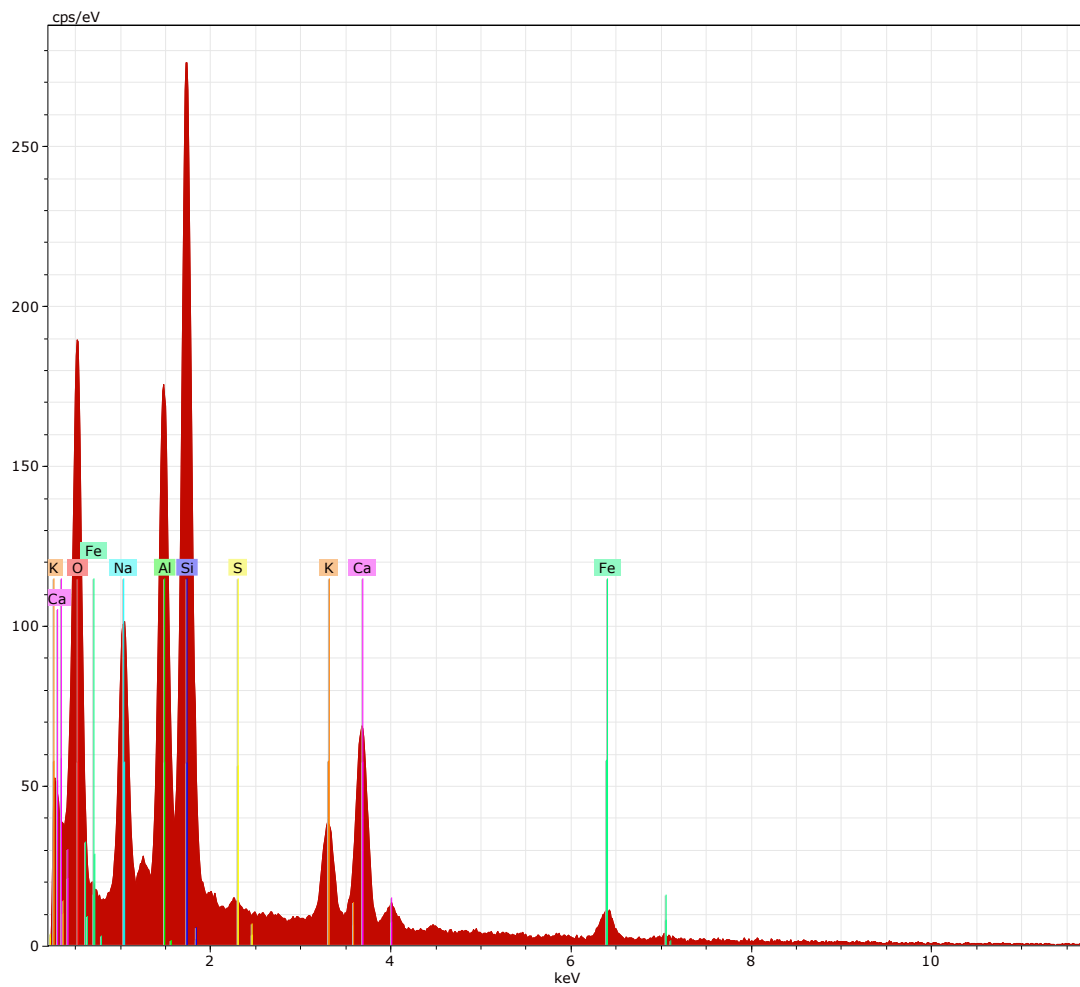
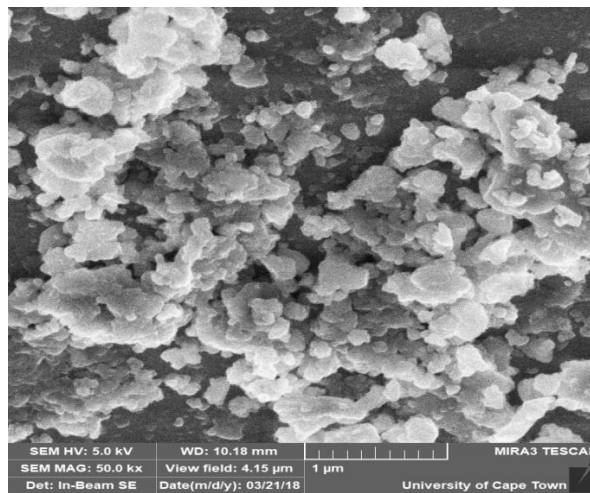


Peak List
Nepheline; Na _{2.8} K _{0.6} Ca ₂ Al _{3.8} Si _{4.2} O ₁₆
Trona; Na ₃ H (C O ₃) ₂ (H ₂ O) ₂
Pirssonite, syn; Ca Na ₂ (C O ₃) ₂ (H ₂ O) ₂
Nyerereite; (Na _{0.82} K _{0.18}) ₂ Ca (C O ₃) ₂
Calcite; Ca C O ₃
Hexahydrate, syn; Mg S O ₄ · 6 H ₂ O
Augite; Ca (Mg _{0.70} Al _{0.30}) (Si _{1.70} Al _{0.30}) O ₆
Nahcolite; Na H C O ₃
Bornite; Cu _{4.98} Fe _{1.02} S ₄

Appendix 3: Surface morphology and EDS compositions of OLA-TP-850 sample before adsorption.



Appendix 4: Surface morphology and EDS compositions of OLA-TP-850 sample after adsorption.



RESEARCH OUTPUT

Journal Article

Paper 1: Oldoinyo Lengai Volcanic Ash for Removal of Hydrogen Sulfide and Ammonia from Biogas.


Kandola, I., Pogrebnoi, A. and Pogrebnaya, T. (2018). Oldoinyo Lengai Volcanic Ash for Removal of Hydrogen Sulfide and Ammonia from Biogas. *Journal of Materials Science and Chemical Engineering*. **6(04)**: 78-93.


Poster Presentation

REMOVAL OF HYDROGEN SULFIDE AND AMMONIA FROM BIOGAS USING OLDOINYO LENGAI VOLCANIC ASH

Isack Kandola and Prof. Alexander Pogrebnoi

The Nelson Mandela African Institution of Science and Technology





Introduction

The removal of H₂S and NH₃ as toxic components from the biogas stream is an important environmental issue which many researchers focused on globally (Karmakar *et al.*, 2015). The hydrogen sulfide in biogas causes corrosion of metal components, such as regulators valves, gas meters, and mountings. Also, combustion of biogas containing H₂S produces poisonous sulfur dioxide (SO₂), which dissolves in engine oil causing the oil to become acidic and lose its ability to lubricate (Nicolas and Steve, 2009). Ammonia (NH₃) in biogas stream when released free to the atmosphere, it endures a number of chemical reactions troubling the atmospheric equilibrium. Removal of H₂S and NH₃ from the biogas stream is very important for equipment protection. The Oldoinyo Lengai is the only active atocarbonatites volcano and it is unique source of alkaline ash in the world. The OLA is abundant and readily available; its composition has been critically characterized and analyzed (Rowe *et al.*, 1996; Carmody, 2012, Bremner and Banwart, 1976; Carmody *et al.*, 2013). The study aims at investigating the potential of Oldoinyo Lengai volcanic ash (OLA) in removing hydrogen sulfide from biogas plants at ambient temperature.

Specific Objectives

- Collection, preparation and characterization of samples.
- Measurements of H₂S and NH₃ removal.
- The evaluation of influence of height the samples were collected, calcination temperature, flowrate, and mass of adsorbent on the sorption capacity.

Significance of the Study

- Provision of clean biogas for industrial and domestic use.
- Minimizing the effects caused by H₂S and NH₃.
- To add more option to existing methods by utilizing Oldoinyo Lengai ashes which are abundant and locally available.

Figure 1: XRD patterns for OLA-TP-850 sample (a) before and (b) after adsorption.

(ii) SEM Analysis

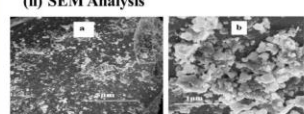


Figure 2: Surface morphology of OLA-TP-850 sample (a) before and (b) after adsorption.

Methodology

Collection, drying and grinding of Oldoinyo Lengai Ashes

Calcination at temperature T_c 550, 650, 750 and 850 °C

Adsorption of H₂S and NH₃ from biogas using the OLA at Banana Investment Ltd Arusha

Figure 3: Effect of calcination temperature on removal efficiency of H₂S (a) and NH₃ (b); OLA-TP samples, flowrate 0.002 m³/min, mass of the adsorbent 1 g.

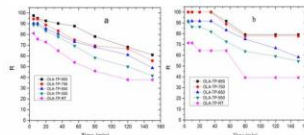
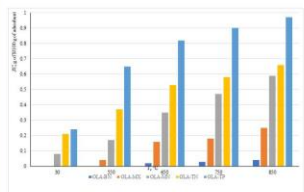


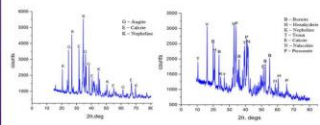
Figure 4: Sorption capacity of Oldoinyo Lengai ash materials for hydrogen sulfide removal.



Results

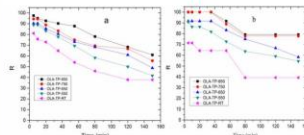
I. Characterization

(i) XRD Analysis



(a) (b)

2. Adsorption



Conclusions

- The calcinated OLAs samples possess high adsorption efficiency of removing H₂S and NH₃ from biogas.
- Chemisorption of H₂S was confirmed via bornite (Cu₅FeS₄) and hexahydrite (MgSO₄ · 6H₂O) formation after sorption, while CO₂ and NH₃ removal was confirmed via trona Na₃H(CO₃)₂(H₂O)₂, pirssonite CaNa₂(CO₃)₂(H₂O)₂ and nahcolite NaHCO₃ formation.

Objectives

General Objective

Evaluation of the performance of Oldoinyo Lengai volcanic ash in the hydrogen sulfide and ammonia removal from biogas.

Selected references

Karmakar, M. K., Chandra, P. and Chatterjee, P. K. (2015). A review on the fuel gas cleaning technologies in gasification process. *Journal of Environmental Chemical Engineering*. **3(2)**: 689-702.

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Nicolas, A. and Steve, B. (2009). A review of biogas purification processes. *Biofuels, Bioproducts and Biorefining*. **3(1)**: 42-71.

Oldoinyo Lengai Volcanic Ash for Removal of Hydrogen Sulfide and Ammonia from Biogas

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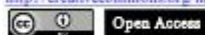
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Abstract

Oldoinyo Lengai mountain located in Northern Tanzania is the only active natrocarbonatite volcano with unusually alkali-rich natrocarbonatites which are not found elsewhere in the world. Volcanic ash formed earlier during eruptions was collected from different sites along the mountain, and its potency to adsorb hydrogen sulfide (H₂S) and ammonia (NH₃) from biogas was investigated. The samples were calcinated at different temperatures (550°C - 850°C) and were characterized by X-ray florescent, scanning electron microscopy and X-ray diffraction techniques. The on-site adsorption experiments were conducted at the biogas digester at ambient conditions. The calcinated ash was packed into the reactor bed, biogas allowed to pass through the adsorbent, and the inlet and outlet concentrations of H₂S and NH₃ were measured. The height of the site where the adsorbent was taken from, calcination temperature, biogas flowrate and mass of the adsorbent were variable parameters and found to influence greatly on the efficiency of H₂S and NH₃ removal. The efficiency is increased with calcination temperature raise and mass of adsorbent and decreased with flowrate increase. The samples collected from the top site of the mountain and calcinated at 850°C exhibited the best sorption performance.

Keywords

Adsorption, Calcination, Flowrate, Oldoinyo Lengai, Volcanic Ash, H₂S and NH₃ Removal

1. Introduction

Biogas produced by waste biomass becomes one of the vital substitute energy sources in recent years as it is obtained from non-fossil fuels [1]-[7]. The biogas consists of CH₄ and CO₂ which are the main constituents, but also contains in-

sufficient amount of contaminants such as H_2S , NH_3 , siloxanes and halogenated volatile organics [8] [9] [10] [11]. The hydrogen sulfide in biogas stream stands as extremely toxic gas which causes corrosion, erosion, fouling for metal devices such as, cooking stoves, biogas plants and steam turbines [12]. The presence of H_2S in combustion process results in formation of sulfur dioxide which is harmful for environment [13] [14], and injurious for human and animal health as it causes irritation of mucous membranes, headaches, dizziness, nausea and sudden death. For these motives, substantial attention has been paid to removal of H_2S from biogas stream prior to use.

Researchers focused on developing methods of H_2S removal from biogas stream. These methods are mainly directed in fabrication of various materials to adsorb and capture H_2S from gas streams [8] [9] [10] [11] [13] [15]-[21]. Currently, biogas sequestration through the adsorption process is a striking method due to its simplicity and low-cost materials such as natural clay soils and red mud soils [19] [20] [22] [23] [24] rich with iron oxide; the latter being oxidizing agent to convert H_2S to elemental sulfur which is a vital factor for biogas sequestration. Meanwhile, few studies have proposed the utilization of waste ashes (coal ash, biomass ash) [15] [25] [26] [27] [28], kaolin and modified crude clay [29] [30], Pennausende muscovite [31], laterite [32], montmorillonite [33] [34], which are economically feasible for CO_2 and H_2S removal.

Considering many benefits of biogas use as non-fossil fuel, it is imperative to develop cost effective adsorbents, easy way of removing toxic substances for application at medium and small-scale plants. Hence this current study aiming to investigate the removal of H_2S and NH_3 from biogas using Oldoinyo Lengai volcanic ash (OLA) at ambient temperature conditions. The Oldoinyo Lengai is the only active natrocarbonatite volcano and it is a unique source of alkaline ash in the world; the OLA is abundant and readily available [35] [36] [37] [38]. The experiment was conducted on-site at The Banana investment company Ltd, Arusha, Tanzania where characteristics of H_2S and NH_3 removal from biogas stream were determined at natural variation of biogas composition.

2. Materials and Methods

2.1. Materials Collection and Preparation

Ashes used in this study were collected from Oldoinyo Lengai volcano which is located Tanzania, the Rift Valley at 2°45'S, 35°55'E and 2000 m above the Serengeti plains [35] [37]. Several samples of ashes were randomly collected from various places on top, medium and bottom of the mountain. Previously it was found that the samples contain compounds of K, Na, Ca, Zn and Fe [15] [38] [39] [40] which are potentially effective for H_2S and NH_3 removal from biogas stream. The OLA samples were air dried, ground with a mortar and pestle, sieved to obtain the acquired particle size, below 2 mm, and stored in vacuum desiccators until used. The samples were calcinated at different temperatures 7, 550°C, 650°C, 750°C, and 850°C for one hour in the oven (Thermo Scientific

1200 Box furnace) and then allowed to cool; the heating rate was 10°C/min and cooling rate 20°C/min. After the preliminary test on H₂S removal was performed, the best samples were retained for further investigations and detailed experiments. The selected samples were two from the top (OLA-TP and OLA-TN), two from medium (OLA-MN and OLA-MX) and one from bottom (OLA-BN), where TP and TN represent white ashes without and with plants, respectively; MN is white with plants and MX is a mixture of black and white ashes with plants. The notation of the samples also includes the calcination temperature, e.g. OLA-TP-850 implies the sample was collected at the top site of the mountain and calcinated at 850°C. The raw materials taken at room temperature (30°C) are denoted as OLA-TP-RT.

2.2. Materials Characterization

The oxides composition of the samples was determined by X-ray fluorescence spectrometer (XRF), model MiniPal4 (Pw4030)-Rh manufactured by PANalytical, using software provided with the instrument. A sample of 25 g of calcinated adsorbent was added to 100 ml of distilled water. The mixture was stirred and shaken for one hour by using mechanical shaker (model AS200, RETSH Company). The pH of samples was measured with a pH meter, model H199121. The moisture content of raw OLA ashes determined under standard procedures as has been reported elsewhere [32] [41] was found to be 22.2% ± 0.5%. Mineral phase analysis and elemental oxide composition were analyzed by X-ray diffraction (XRD) technique using D2 phaser-Bruker model and X-ray diffraction meter with a Cu-K_α radiation source in a 2θ range between 10° and 80° at a scanning rate of 2° min⁻¹ and analyzed using EVA software provided with the instrument.

The surface micromorphology of samples was investigated using a scanning electron microscope (SEM), modal JEOL JSM-6335F with resolution of 500 nm, at 200 kV at the Department of Materials Science and Engineering, University of Connecticut, USA.

2.3. Measurements of H₂S and NH₃ Removal and Evaluation of Sorption Capacity of Adsorbents

The sorption experiment of H₂S and NH₃ was carried out at the Banana Investments company Ltd in Arusha, Tanzania where the biogas was produced from winery effluent banana industrial waste. The biogas was liberated from upflow anaerobic sludge blanket between 100 and 120 m³ daily, the composition of the gas was determined with the biogas 5000 g as analyzer to be 82% - 89% CH₄, 12% - 15% CO₂, <1% O₂, 5 - 48 ppm of NH₃, and 24 - 60 ppm of H₂S [42].

A reactor made of plastic tube, 6.5 cm length, 1.7 cm diameter, filled with adsorbent supported by cotton wool on both end sides of the reactor tube. The biogas allowed to flow through the reactor at ambient temperature varying the flowrate from 0.0004 to 0.008 m³/min, and mass of adsorbents from 0.5 to 2.0 g.

The mass of adsorbent of 1 g and the biogas flowrate of 0.002 m³/min were used as standard parameters for this study. Schematic diagram and photos of the experimental setup are shown in **Figure 1**. The flowrate was controlled and monitored by using a flow meter, model JBD2.5-SA. The concentration of H₂S and NH₃ was recorded at the inlet and outlet of the reactor with different time intervals from 5 to 150 min. Breakthrough time (*BT*) was noted when the outlet concentration C_{out} of H₂S and NH₃ reached 50% of the inlet concentration C_{in} . The sorption tests were repeated at least twice for each sample.

The performance of material adsorbent was specified as percentage removal R :

$$R = \frac{C_{in} - C_{out}}{C_{in}} \times 100 \quad (1)$$

Sulfur sorption capacity (SC) of the OLA samples, in grams of sulfur per 100 grams of sorbent, was determined as described in [16] [43] [44]:

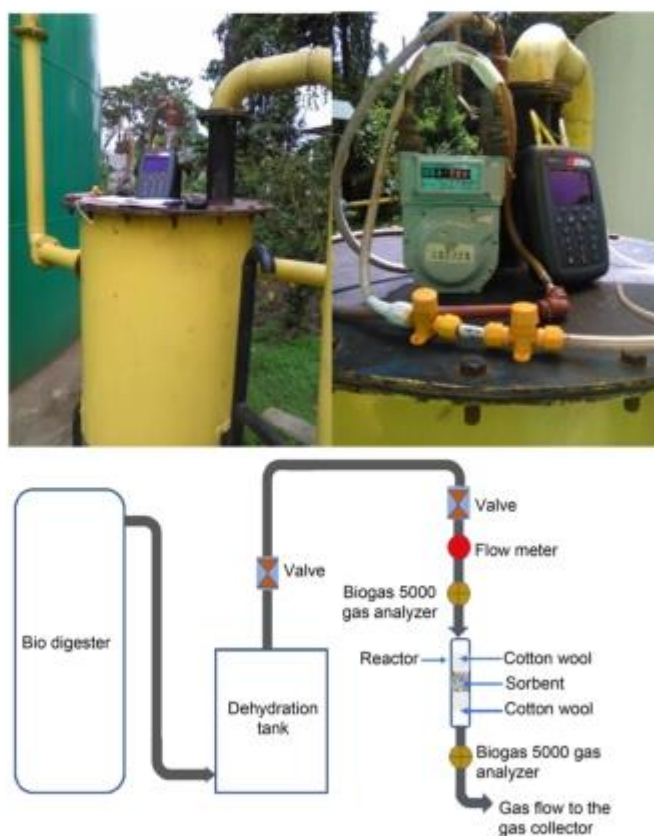


Figure 1. Photos and schematic diagram of the sorption experimental setup.

$$SC = GHSV \times \left[\frac{M}{V_{mol}} \times \int_0^t (C_{in} - C_{out}) dt \right], \quad (2)$$

where *GHSV* is the gas hourly space velocity which is the volume of the gas flowing hourly through the reactor with 1 g of absorbent ($L \cdot h^{-1} \cdot g^{-1}$); V_{mol} is the molar volume of the gas ($L \cdot mol^{-1}$) under standard conditions, *M* is the atomic mass of sulfur; C_{in} and C_{out} are the H_2S concentrations before and after sorption (ppm); *t* is the breakthrough time in hours.

3. Results and Discussion

3.1. XRF Analysis and pH of Raw OLA Samples

Results on the XRF analysis of the raw OLA samples (Table 1) show that Fe_2O_3 , CaO and SiO_2 are most abundant components of all samples; alkali metal oxides are in essential amount, K_2O ~3% - 10% and Na_2O ~2% - 5%. Some of transition and rare-earth elements were also found. As is seen the content of these oxides changes with height the samples were collected. The composition of the OLA samples is rather promising for H_2S removal due to, as it was observed earlier [15] [41] [45], Fe, K, Ca, Zn, Na, Ti, and Sr oxides may act as catalysts for oxidation of H_2S .

The pH values of the OLA ashes are in the range of about 11 - 12 and indicate materials' alkalinity which is evidently caused, according to [39], by presence of iron, calcium, potassium and sodium compounds. The basicity of the OLA ashes is expected to favour the hydrogen sulfide removal as it was shown for example in [45]. The mixed metal fly ashes [15] [25] [45], different metal oxides [15] [31] [33] [41] [46] [47] [48], coal ashes [15] [49] were successfully used for H_2S

Table 1. The composition (wt%) and pH values of Oldoinyo Lengai volcanic ash samples.

Oxides	OLA-TP	OLA-TN	OLA-MN	OLA-MX	OLA-BN
Fe_2O_3	25.40	24.60	24.40	24.60	21.10
K_2O	5.40	2.80	9.71	2.82	4.29
CaO	46.00	46.00	36.80	36.50	36.00
ZnO	0.20	0.13	0.20	0.10	0.10
Al_2O_3	5.60	1.30			1.90
SiO_2	5.10	11.00	19.40	21.20	24.00
TiO_2	2.40	2.50	2.78	2.62	2.99
BaO	1.30	2.00	1.00	1.80	1.30
Na_2O	5.10	3.90	2.40	3.10	5.30
SrO	2.80	2.27	2.25	3.08	2.02
Eu_2O_3	0.39	0.39	0.27	0.38	0.58
Nb_2O_5	0.27	0.24	0.40	0.25	0.20
MoO_3	0.04		0.07		
Total	100	97.13	99.68	96.45	99.78
pH	12.31	11.04	10.91	11.01	11.06

removal from biogas stream at ambient temperature.

The mechanism of the H_2S adsorption/oxidation processes was considered in [3] [12] [50] [51]; it was shown that inorganic materials containing active metal oxides participate in this process. The H_2S was oxidized to sulfur due to presence of moisture, which enabled dissociation of H_2S into HS^- and then to elemental sulfur. These reactions were enhanced by basic pH of the adsorbent [3] [48].

3.2. XRD Analysis of Calcinated OLA Samples

The XRD spectra were measured for several samples; an example for the OLA-TP-850 is shown in **Figure 2**. The data indicate the crystalline solid form of the materials where compounds of iron, sodium, calcium and potassium are identified as main components by peaks of magnetite ($2\theta = 35.5^\circ, 43^\circ, 57^\circ, 63^\circ$), analcime ($2\theta = 16^\circ, 18^\circ, 26^\circ$), epidote ($2\theta = 31^\circ, 56^\circ$) and nepheline ($2\theta = 21^\circ, 23^\circ, 27^\circ, 29.8^\circ, 37^\circ$), respectively. These results are in accordance with the data reported previously [39]. For the sample after absorption, the additional peaks were recorded at $2\theta = 22^\circ, 31^\circ, 32.5^\circ$ and 49° which correspond to sodium hydrogen sulfate $Na_2H(SO_4)_2$. The formation of this compound indicates interaction of hydrogen sulfide with the adsorbent and hence chemisorption occurrence. Our results differ from those published [19] in which red mud was used for H_2S removal, and after sorption FeS_2 , FeS , $CaSO_4 \cdot 2H_2O$, sulfur, sodium sulfide and bisulfide were formed.

Apparently, the distinction of our results with literature [19] may be attributed to the different mineralogical and chemical composition of the adsorbents.

3.3. SEM Surface Micromorphology Analysis

The surface morphology of samples was investigated using SEM; an example shown in **Figure 3** for OLA-TP-850. The surface features indicate considerable

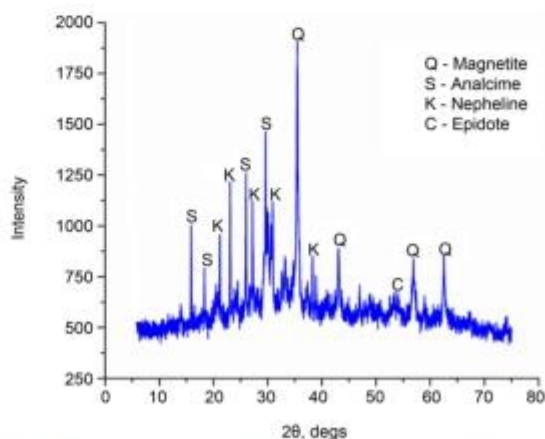


Figure 2. XRD patterns for OLA-TP-850 sample before adsorption.

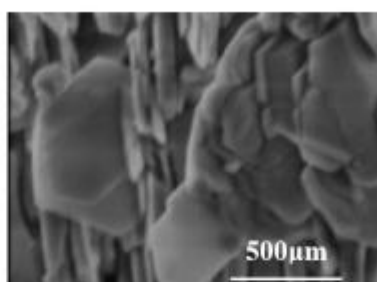


Figure 3. Surface morphology of OLA-TP-850 sample before adsorption.

porosity which evidently may provide efficient physisorption.

It was observed earlier that the porous structure and surface chemistry of the adsorbent had significant effect on adsorption and oxidation of hydrogen sulfide [33]. Besides the morphology of ashes is controlled by calcination temperature, and porosity increases with T_c increase [51]. We may expect that our samples which were calcinated at higher temperatures would demonstrate better adsorption performance.

3.4. Adsorption Performance of OLA Samples

3.4.1. Effect of Calcination Temperature and Height the Samples Were Collected

The values of sorption capacity calculated using Equation (2) and breakthrough time are given in **Table 2** for different OLAs. The effect of calcination temperature and height of sites the samples were collected on the sorption capacity is depicted also in the diagram (**Figure 4**). As is seen, the SC is increased with calcination temperature raise; e.g., the ashes taken without calcinations, OLA-TP-RT, and calcinated at 850 °C, OLA-TP-850, result in the SC of ~0.2 and ~1.0 g S/100g of adsorbent, respectively. It is also observed that the SC increases with height of site; the samples collected at the top and calcinated at 850 °C, OLA-TP-850, demonstrate the best performance. The breakthrough time relates to the life time of the adsorbent; the longer is the BT , the higher is the working capability of the material. One can see the BT increases greatly with height (from 5 min for OLA-BN-650 to 120 min for OLA-TN-650) and calcination temperature raise (from 55 min for the OLA-TP-RT up to 177 min for OLA-TP-850). Thus, the OLA-TP-850 samples possess the longest working time.

The adsorption efficiency removal R was measured both for H_2S and NH_3 and analyzed for different samples with respect to time interval between the measurements of initial and final concentrations of the adsorbates while biogas flowed through the reactor. The plots for R vs time for the samples collected at different heights and calcinated at 850 °C are shown in **Figure 5**. Results indicate the removal efficiency decreases with time for all samples. For the OLA-TP-850, R reduces by ~10% both for H_2S and NH_3 after one hour of the adsorbent's use.

Table 2. Adsorption performance of different OLA samples for H₂S removal: sorption capacity and breakthrough time; mass of adsorbent 1 g and the biogas flowrate 0.002 m³/min.

Sample	SC, g of S/100g of adsorbent	BT, min
OLA-TP-RT	0.24	55
OLA-TN-RT	0.21	35
OLA-MN-RT	0.08	20
OLA-TP-550	0.65	120
OLA-TN-550	0.37	80
OLA-MN-550	0.17	35
OLA-MX-550	0.05	10
OLA-TP-650	0.82	150
OLA-TN-650	0.53	120
OLA-MN-650	0.35	80
OLA-MX-650	0.16	35
OLA-BN-650	0.02	5
OLA-TP-750	0.90	165
OLA-TN-750	0.58	150
OLA-MN-750	0.47	120
OLA-MX-750	0.18	35
OLA-BN-750	0.03	5
OLA-TP-850	1.00	177
OLA-TN-850	0.67	150
OLA-MN-850	0.59	120
OLA-MX-850	0.25	55
OLA-BN-850	0.04	10

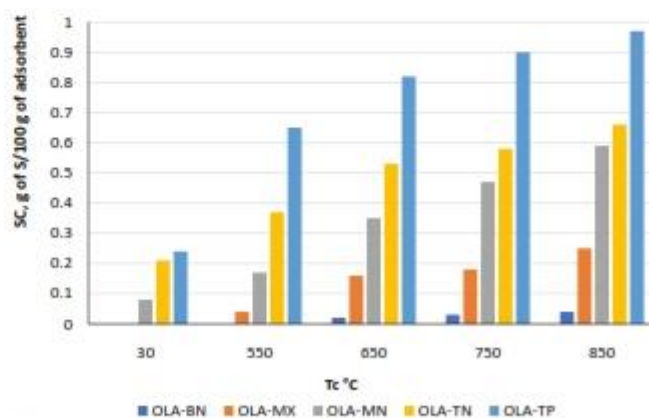


Figure 4. Sorption capacity of Oldoinyo Lengai ash materials for hydrogen sulfide removal; mass of adsorbent 1 g and the biogas flowrate 0.002 m³/min.

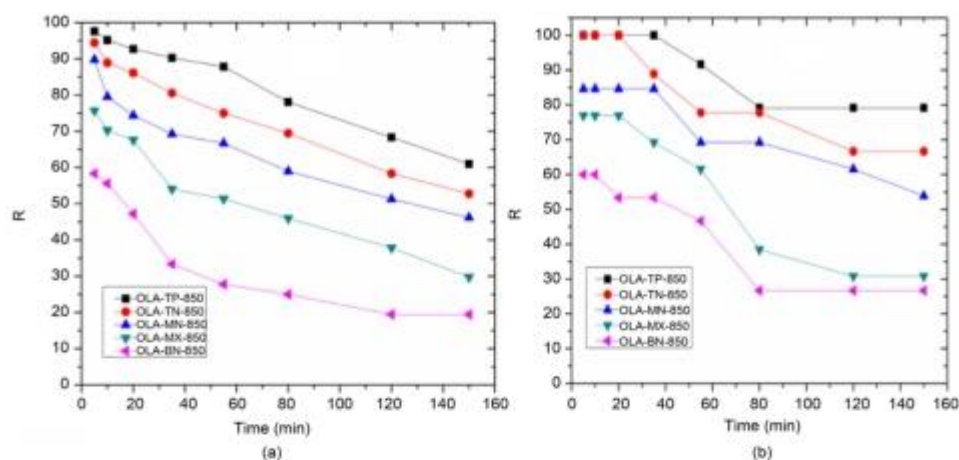


Figure 5. Effect of the site location on the removal efficiency of H_2S (a) and NH_3 (b); for all samples $T_c = 850^\circ C$, flowrate $0.002 \text{ m}^3/\text{min}$, mass of the adsorbent 1 g .

Similar trend is observed in **Figure 6** where the plots of R vs time are given for OLA-TP samples calcinated at different temperatures. The removal efficiency is increased with calcination temperature raise. Thus after 150 min of the adsorbent's use, the R of OLA-TP-RT descends to 37%, while the OLA-TP-850 holds 60% for H_2S removal; for ammonia, the values of R are 40% and 80%, respectively. Based on the results of [33] [52] [53], we suggest that the increase in adsorption efficiency with temperature T_c may be caused by increase of number of pores created in adsorbents. On the other hand, the removal efficiency decreases in time because the surface of adsorbent is being occupied with the adsorbate molecules and the porosity is reduced as the pores are clogging with the gas molecules [32].

If compare the plots of R vs time for H_2S and NH_3 , they look differently: monotonic decay for the former and step-like for latter. The step-like behavior for ammonia may be attributed to rather low concentration ($C_{in} \sim 0.005 \text{ mg } NH_3 \text{ per } 1 \text{ g}$ of the biogas, that is one order less than of H_2S) measured at the sensitivity limit of the gas analyzers. Moreover, according to Equation (2), the lower input concentration of ammonia also brings bigger value of R .

Therefore, among all OLA samples considered the ashes collected at the top site and calcinated at $850^\circ C$, the OLA-TP-850, demonstrated the best removal efficiency retaining it high during the exploitation time of the adsorbent.

3.4.2. Effect of Biogas Flowrate

The effect of biogas flowrate on the samples adsorption performance was investigated; the flowrates were 0.0004 , 0.001 , 0.002 , and $0.008 \text{ m}^3/\text{min}$. The values of the removal efficiency of H_2S and NH_3 are plotted vs time for the top-site samples OLA-TP-850 in **Figure 7**. One can see, with the flowrate raise from 0.0004

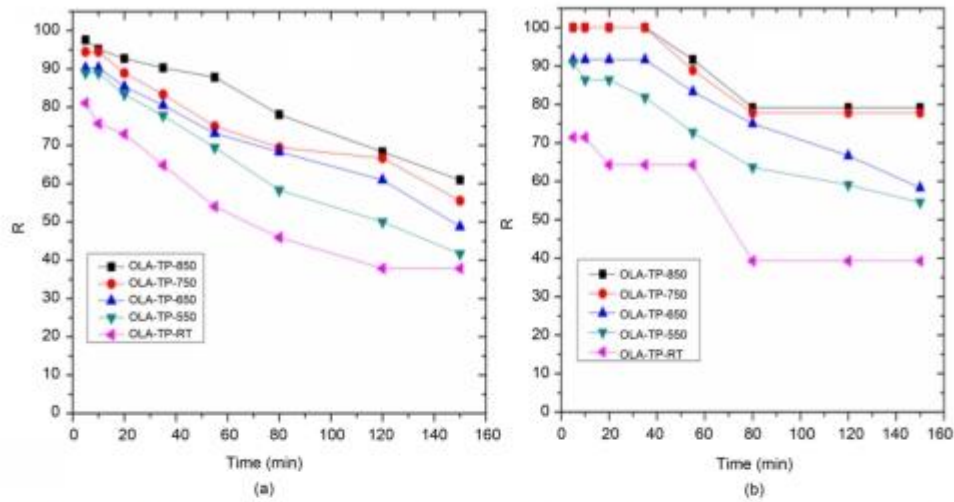


Figure 6. Effect of calcination temperature on removal efficiency of H_2S (a) and NH_3 (b); OLA-TP samples, flowrate $0.002 \text{ m}^3/\text{min}$, mass of the adsorbent 1 g .

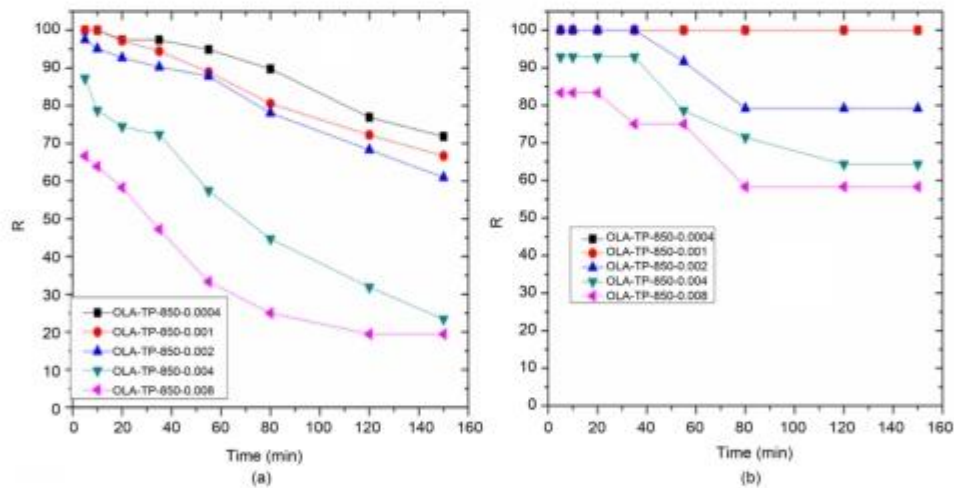


Figure 7. Effect of biogas flowrate on removal efficiency of H_2S (a) and NH_3 (b); OLA-TP-850, mass of the adsorbent 1 g .

to $0.008 \text{ m}^3/\text{min}$ the R values decrease from 71% to 20% for H_2S and from 100% to 58% for NH_3 , respectively, measured after 150 min adsorbent's use.

It seems at low flowrate ($0.0004 \text{ m}^3/\text{min}$) the materials get enough contact time for interaction between gas molecules and adsorbent; whereas at high flowrate ($0.008 \text{ m}^3/\text{min}$), H_2S and NH_3 gas molecules can pass through without being adsorbed and reacted fully with adsorbent. Therefore, the contact time be-

tween gas and adsorbent is significant in determining the adsorption capacity. This is in accordance with findings reported in [48].

3.4.3. Effect of Mass of Adsorbent Material

The effect of variation of the adsorbent mass, from 0.5 to 2.0 g, on the removal efficiency of H_2S and NH_3 , was considered for the samples OLA-TP-850 (Figure 8). The results indicate that R values evidently increase with mass. Four-fold enlargement in mass leads to essential increase in removal efficiency, from 23 to 80% for H_2S and from 50% to 100% for NH_3 , measured after 150 min adsorbent's use. When the mass of adsorbent was 2 g, the material retained 100% H_2S removal after 40 min and efficiency decreased to 80% after 150 min; while for NH_3 , the adsorbent held 100% removal efficiency for all time measurements.

3.4.4. Comparison of OLA-TP-850 with Other Materials

The adsorption properties of our best sample OLA-TP-850 are compared to other materials reported in literature (Table 3).

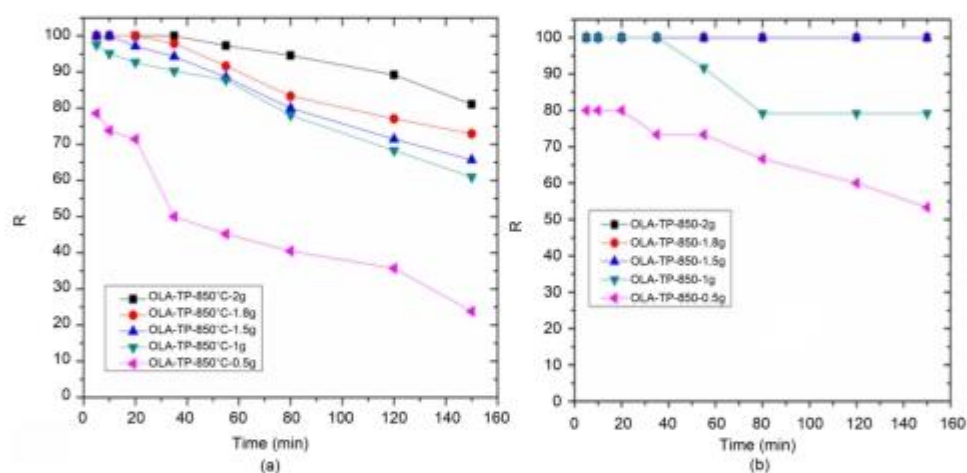


Figure 8. Effect of adsorbent mass on removal efficiency of H_2S (a) and NH_3 (b); OLA-TP-850, flowrate $0.002 \text{ m}^3/\text{min}$.

Table 3. Adsorption properties of OLA-TP-850 compared to other materials.

Adsorbent	Mass, g	Biogas flowrate, m^3/min	H_2S removal, g S/100g of adsorbent	pH	Ref.
Moist soils	1 - 5	8.00×10^{-4}	0.50	5.70 - 7.70	[54]
Montmorillonite clay	12.50	51.00×10^{-2}	1.27	9.00	[33]
Municipal waste bottom ash	13×10^4	55.94×10^{-3}	0.30	9.80	[55]
Red mud soil	5	5×10^{-1}	2.10	>13.00	[19]
Coal ashes	10	14.20×10^{-3}	0.50	11.90 ± 0.01	[15]
OLA-TP-850	1	2×10^{-1}	1.00	12.31	Current study

The sorption capacity of OLA ashes appeared to be close to the commercial montmorillonite clay and higher than other natural materials used for H₂S removal, e.g. municipal waste bottom ash, coal ashes etc. Meanwhile, when different samples are compared it is worth to take into account the effect of experimental conditions like the biogas flowrate and pH; as it was mentioned above, the lower flowrate and basicity of the sorbent favour the hydrogen sulfide removal. Thus, the Oldoinyo Lengai volcanic ashes can be used as adsorbents for H₂S and NH₃ removal in biogas plant industries, however further improvement of the adsorption properties may be suggested, e.g., increasing of calcination temperature and activation with chemical reagents.

4. Conclusion

A potency of the Oldoinyo Lengai volcanic ashes on removal of hydrogen sulfide and ammonia from biogas stream was investigated. Sorption capacity and removal efficiency were measured for different OLA samples at ambient temperature. The materials were examined in the on-site experiment at real industrial conditions. The best materials demonstrated long-lasting sorption ability. The XRD and XRF spectra of the OLA samples were examined. Mineralogical composition analysis exhibited an abundance of compounds of iron, alkali and alkali-earthmetals; rare-earth metals compounds were also found. The high porosity of samples favoured physisorption of H₂S and NH₃. Moreover, chemisorption of H₂S was confirmed *via* formation of sodium sulfate-sodium bisulfate. In our on-site experiment the biogas flowrate and mass of adsorbent were variable parameters. The inlet concentration of H₂S in biogas was controlled but difficult to keep constant. For the next step, it may be recommended to evaluate the effect of concentration of H₂S and NH₃ on the sorption capacity of the samples in laboratory conditions.

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Conflict of Interest

The authors have not declared any conflict of interest.

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