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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 (H<sub>2</sub>S) and ammonia (NH<sub>3</sub>) 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 H<sub>2</sub>S and NH<sub>3</sub> 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 H<sub>2</sub>S and NH<sub>3</sub> 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 m<sup>3</sup>/min were used as standard parameters for this study. Chemisorption of H<sub>2</sub>S was confirmed *via* bornite and hexahydrite, while CO<sub>2</sub>, confirmed *via* trona, pirssonite and nahcolite while NH<sub>3</sub> 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.



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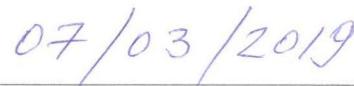


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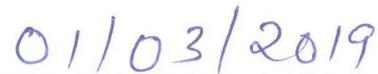
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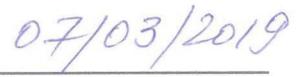
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## CERTIFICATION

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.



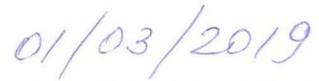
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## **DEDICATION**

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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 <sub>in</sub>	Inlet concentration
C <sub>out</sub>	Outlet concentration
M	Atomic mass of sulfur
T <sub>c</sub>	Calcination temperature

# CHAPTER ONE

## INTRODUCTION

### 1.1 Background of the study

The removal of H<sub>2</sub>S and NH<sub>3</sub> 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 H<sub>2</sub>S produces poisonous sulfur dioxide (SO<sub>2</sub>), which dissolves in engine oil causing the oil to become acidic and lose its ability to lubricate (Nicolas and Steve, 2009). Ammonia (NH<sub>3</sub>) 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, NH<sub>3</sub> forms ammonium salts particles, which interfere with cloud formation and cloud particle circulation (Dämmgen and Erisman, 2005). It also contributes to the formation of NO<sub>2</sub> 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 H<sub>2</sub>S and NH<sub>3</sub> from the biogas stream is very important for equipment protection and environmental conservation (Karmakar *et al.*, 2015). Many materials used for H<sub>2</sub>S 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 H<sub>2</sub>S 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 H<sub>2</sub>S 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 H<sub>2</sub>S 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 H<sub>2</sub>S is through H<sub>2</sub>S 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 H<sub>2</sub>S 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 H<sub>2</sub>S removal from biogas stream. These methods are mainly directed in fabrication of various materials to adsorb and capture H<sub>2</sub>S 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 H<sub>2</sub>S 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 H<sub>2</sub>S 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 H<sub>2</sub>S and NH<sub>3</sub> 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 H<sub>2</sub>S and NH<sub>3</sub> 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 H<sub>2</sub>S 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 H<sub>2</sub>S and NH<sub>3</sub> 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 H<sub>2</sub>S and NH<sub>3</sub> 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 H<sub>2</sub>S 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 H<sub>2</sub>S and NH<sub>3</sub> 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 SO<sub>2</sub>, SO<sub>3</sub> and NH<sub>3</sub> in the atmosphere which cause acid rains.

## CHAPTER TWO

### LITERATURE REVIEW

#### 2.1 Materials for H<sub>2</sub>S removal from biogas

Materials for H<sub>2</sub>S 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 H<sub>2</sub>S and NH<sub>3</sub> 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 H<sub>2</sub>S 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 H<sub>2</sub>S 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 H<sub>2</sub>S 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 H<sub>2</sub>S and NH<sub>3</sub> in biogas stream.

## **2.2 Methods for H<sub>2</sub>S removal**

Methods used in removing of H<sub>2</sub>S 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**

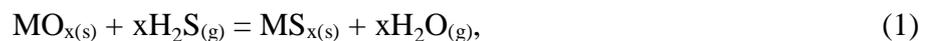
Biotechnological methods include the use of biotrickling filters, *etc.* (Rattanapan and Ounsaneha, 2011), to remove hydrogen sulfide from biogas through aerobic bacteria in bioreactors. Literature indicates that a variety of bacteria applied under anaerobic conditions have ability to oxidize hydrogen 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 H<sub>2</sub>S removal, include acidification of media due to sulfuric acid formation caused by degradation of the H<sub>2</sub>S 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 H<sub>2</sub>S 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 H<sub>2</sub>S removal from biogas at high temperature. The general chemical reaction which describes this procedure is



where MO<sub>x</sub> represents a metal oxide; MS<sub>x</sub> 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 H<sub>2</sub>S from biogas (Huang and Ko, 2015). Also, it has been reported that Fe<sub>2</sub>O<sub>3</sub> from soil is essential candidate showed good efficiency in removing H<sub>2</sub>S from biogas stream even at ambient temperature (Xia *et al.*, 2015; Louhichi *et al.*, 2016).

### 2.3 Performance of materials for removing H<sub>2</sub>S 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 H<sub>2</sub>S 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 H<sub>2</sub>S removal from biogas (Novochinskii *et al.*, 2004).

Iron oxide is the oldest material used to remove H<sub>2</sub>S 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 H<sub>2</sub>S 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 H<sub>2</sub>S by chemical adsorption are alkali-earth metals such as hydrated lime Ca(OH)<sub>2</sub> which reacts with acid gases, H<sub>2</sub>S, CO<sub>2</sub>, through neutralization reaction in a fixed-bed reactor (Nicolas and Steve, 2009). Furthermore, many soils do exhibit a small chemical adsorption capacity for H<sub>2</sub>S that is heavily dependent on the iron content (Bohn, 1989). Red soil contains naturally occurring iron oxides (Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>) and FeOOH which react with H<sub>2</sub>S and CO<sub>2</sub> 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).

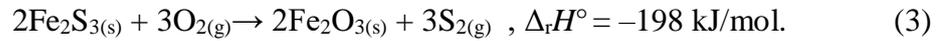
Soil materials contaminated with copper and iron have also been used for removing H<sub>2</sub>S from hot coal gas which involves the reaction between metal oxides and H<sub>2</sub>S (Hu *et al.*, 2012; Huang and Ko, 2015). Literally, the suitability of the performance of materials depends on availability 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 H<sub>2</sub>S 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 H<sub>2</sub>S and NH<sub>3</sub> 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 H<sub>2</sub>S 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 $\alpha$  radiation source in a  $2\theta$  range between  $10^\circ$  and  $80^\circ$  at a scanning rate of  $2^\circ \text{ min}^{-1}$  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 H<sub>2</sub>S and NH<sub>3</sub> removal and evaluation of sorption capacity of absorbents**

The sorption experiment of H<sub>2</sub>S and NH<sub>3</sub> 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 m<sup>3</sup> daily, the composition of the gas was determined with the biogas 5000 gas analyzer to be 82%–89% CH<sub>4</sub>, 12%–15% CO<sub>2</sub>, <1% O<sub>2</sub>, 5-48 ppm of NH<sub>3</sub>, and 24-60 ppm of H<sub>2</sub>S (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 m<sup>3</sup>/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 m<sup>3</sup>/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 H<sub>2</sub>S and NH<sub>3</sub> 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 H<sub>2</sub>S and NH<sub>3</sub> 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<sup>-1</sup>g<sup>-1</sup>);  $V_{mol}$  is the molar volume of the gas (L mol<sup>-1</sup>) under standard conditions,  $M$  is the atomic mass of sulfur;  $C_{in}$  and  $C_{out}$  are the H<sub>2</sub>S concentrations before and after sorption (ppm);  $t$  is the breakthrough time in hours.



Figure 2: Photos of the sorption experimental setup.

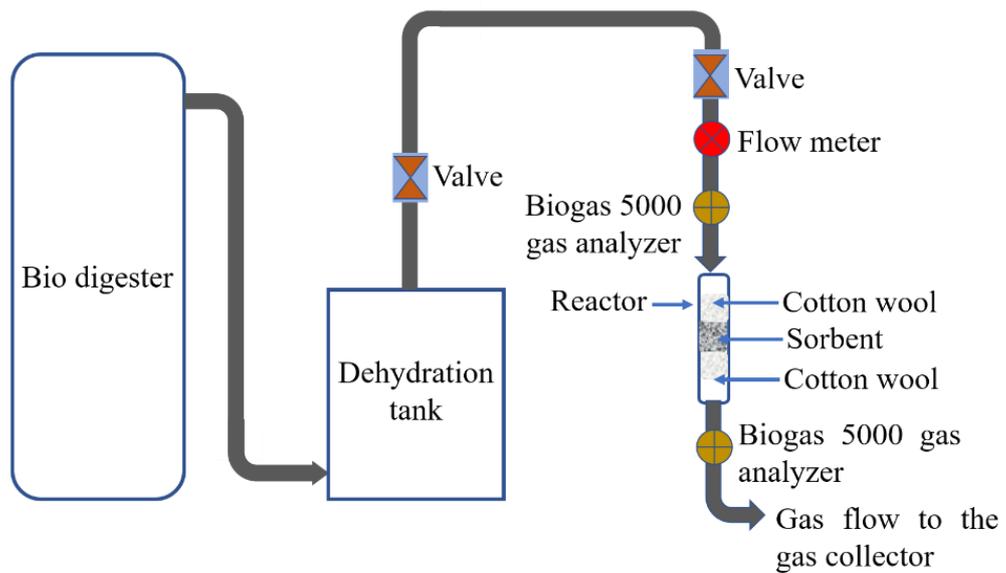


Figure 3: Schematic diagram of the sorption experimental setup.

## 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 Fe<sub>2</sub>O<sub>3</sub>, CaO and SiO<sub>2</sub> are most abundant components of all samples; alkali metal oxides are in essential amount, K<sub>2</sub>O ~3%–10% and Na<sub>2</sub>O ~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<sub>2</sub>S 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 H<sub>2</sub>S.

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 <sub>2</sub> O <sub>3</sub>	25.40	24.60	24.40	24.60	21.10
K <sub>2</sub> 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 <sub>2</sub> O <sub>3</sub>	5.60	1.30			1.90
SiO <sub>2</sub>	5.10	11.00	19.40	21.20	24.00
TiO <sub>2</sub>	2.40	2.50	2.78	2.62	2.99
BaO	1.30	2.00	1.00	1.80	1.30
Na <sub>2</sub> O	5.10	3.90	2.40	3.10	5.30
SrO	2.80	2.27	2.25	3.08	2.02
Eu <sub>2</sub> O <sub>3</sub>	0.39	0.39	0.27	0.38	0.58
Nb <sub>2</sub> O <sub>5</sub>	0.27	0.24	0.40	0.25	0.20
MoO <sub>3</sub>	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 H<sub>2</sub>S removal from biogas stream at ambient temperature.

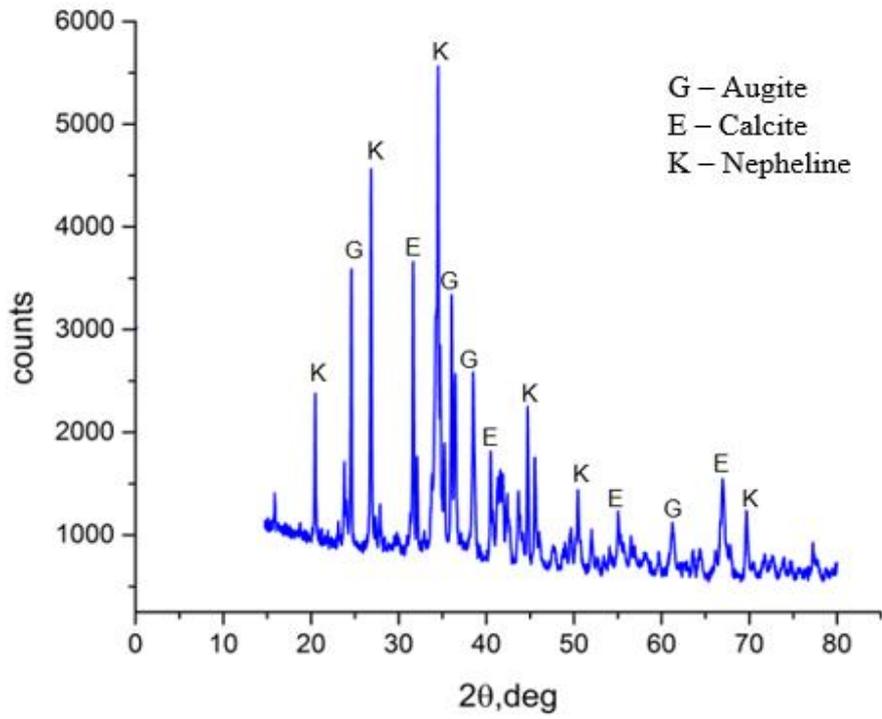
The mechanism of the H<sub>2</sub>S adsorption/oxidation processes was considered in (Adib *et al.*, 1999; Ansari *et al.*, 2005; Bagreev and Bandosz, 2005; Cheng and Liu, 2007); it was shown that inorganic materials containing active metal oxides participate in this process. The H<sub>2</sub>S was oxidized to sulfur due to presence of moisture, which enabled dissociation of H<sub>2</sub>S into HS<sup>-</sup> 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

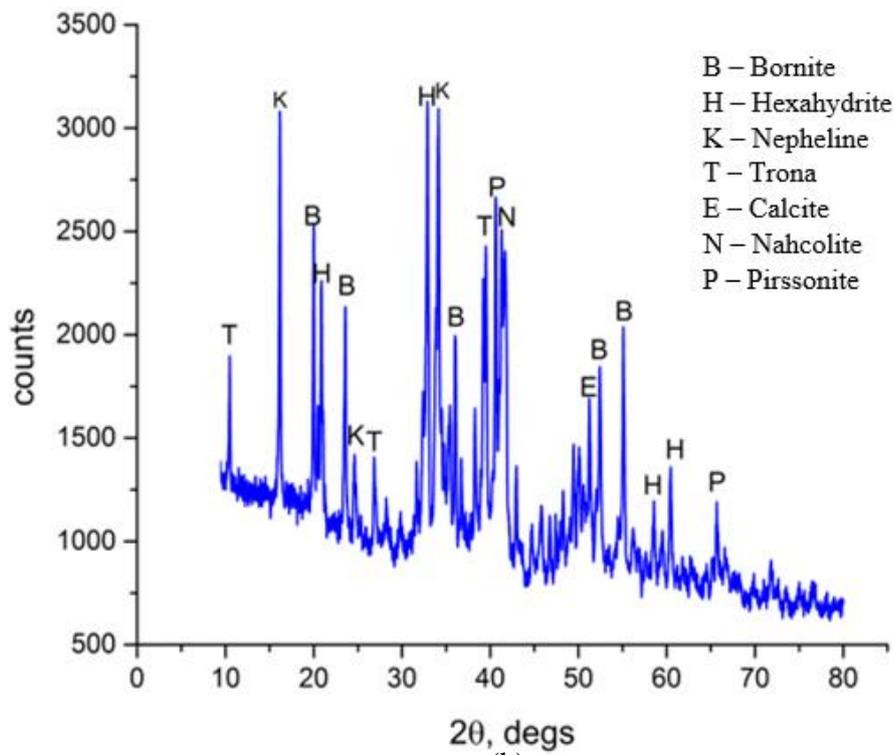
The XRD spectra were measured for several samples; an example for the OLA-TP-850 is shown in Figure 4(a) the data indicate the crystalline solid form of the materials by the peaks of augite Ca(MgAl)(Si<sub>2</sub>Al)<sub>6</sub> has ( $2\theta = 22^\circ, 35^\circ, 38^\circ$ ), calcite (CaCO<sub>3</sub>) has ( $2\theta = 30^\circ, 42.5^\circ, 54.5^\circ, 68^\circ$ ), nepheline (KNa<sub>3</sub>Al<sub>4</sub>SiO<sub>16</sub>) 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 (MgSO<sub>4</sub>·6(H<sub>2</sub>O)) has ( $2\theta = 20^\circ, 34.1^\circ, 58.9^\circ, 59.9^\circ$ ), bornite (Cu<sub>5</sub>FeS<sub>4</sub>) has ( $2\theta = 23^\circ, 25.2^\circ, 34.2^\circ, 55^\circ, 56^\circ$ ) which correspond to the adsorption of H<sub>2</sub>S.

While trona, Na<sub>3</sub>H(CO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>, has ( $2\theta = 10.1^\circ, 26^\circ, 37.9^\circ$ ), pirssonite CaNa<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>, has ( $2\theta = 38.1^\circ, 64^\circ$ ) and nahcolite, NaHCO<sub>3</sub>, has ( $2\theta = 40.5^\circ$ ) correspond to the adsorption of CO<sub>2</sub>, while NH<sub>3</sub> concentration was not seen in the 5000-biogas analyzer after adsorption during measurement at time ranged from 0 to 20 min which implies that NH<sub>3</sub> was completely adsorbed. The NH<sub>3</sub> 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 H<sub>2</sub>S 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.

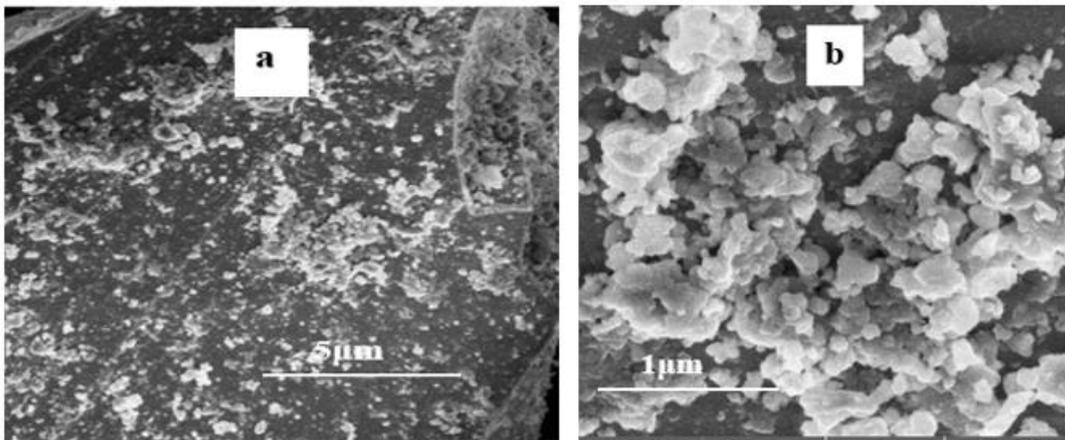


Figure 5: Surface morphology of OLA-TP-850 sample (a) before and (b) after adsorption.

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  $\sim 0.2$  and  $\sim 1.0$  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 H<sub>2</sub>S from gas phase. The H<sub>2</sub>S oxidized to sulfur due to presence of moisture, which enable dissociation of H<sub>2</sub>S into HS<sup>-</sup> 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 H<sub>2</sub>S to elemental sulfur as follows;



Furthermore, common reaction involved the reaction oxidation of H<sub>2</sub>S 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 H<sub>2</sub>S removal: sorption capacity and breakthrough time; mass of adsorbent 1 g and the biogas flowrate 0.002 m<sup>3</sup>/min.

<b>Sample</b>	<b>SC, g of S/100 g of adsorbent</b>	<b>BT, min</b>
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

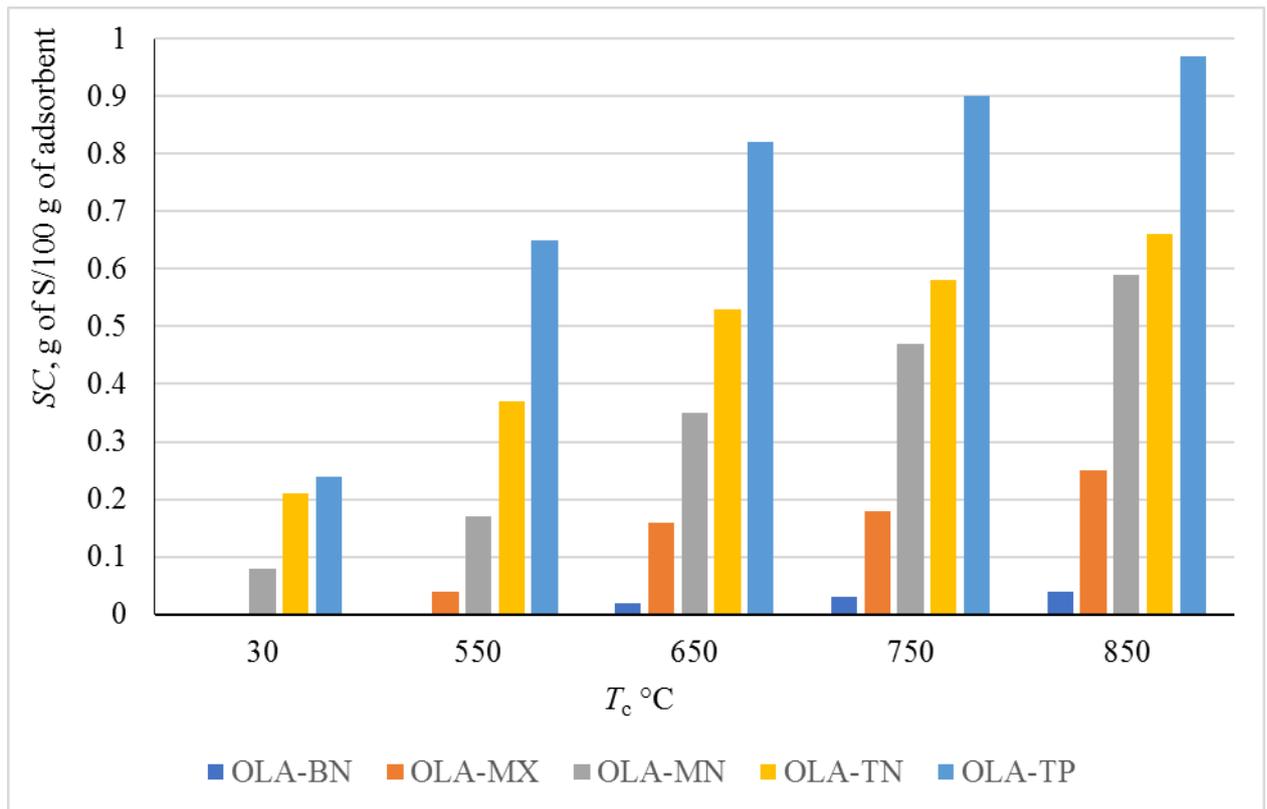


Figure 6: Sorption capacity of Oldoinyo Lengai ash materials for hydrogen sulfide removal.

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 absorbent 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).

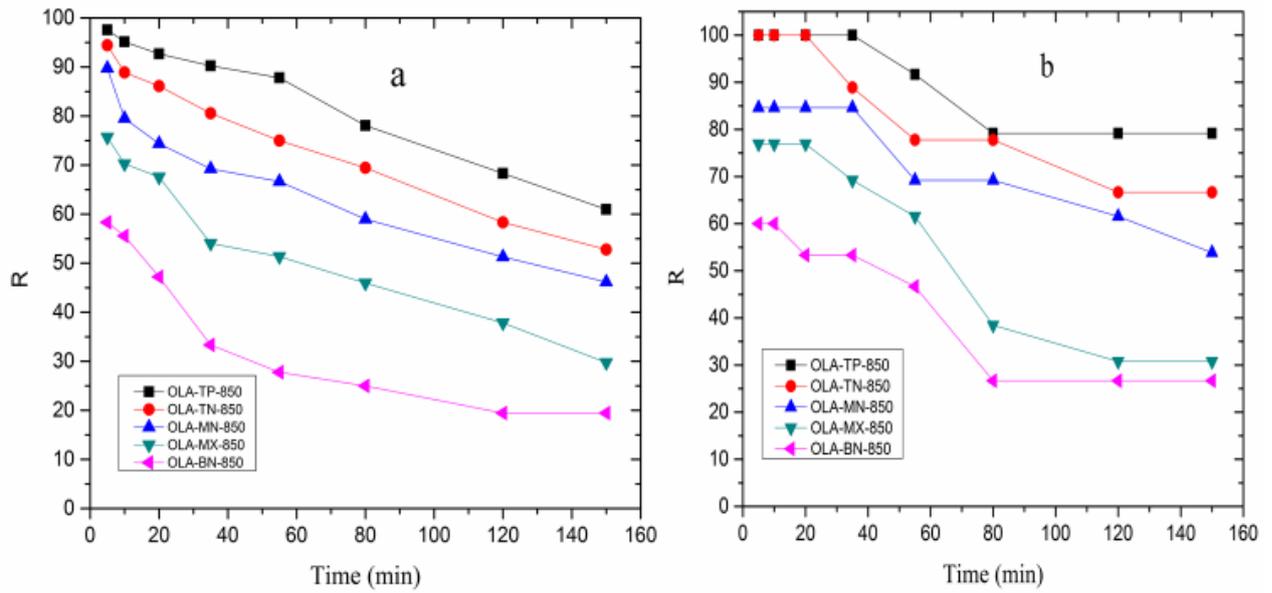


Figure 7: Effect of the site location on the removal efficiency of  $H_2S$  (a) and  $NH_3$  (b); for all samples  $T_c = 850$  °C, flowrate  $0.002$   $m^3/min$ , mass of the adsorbent 1 g.

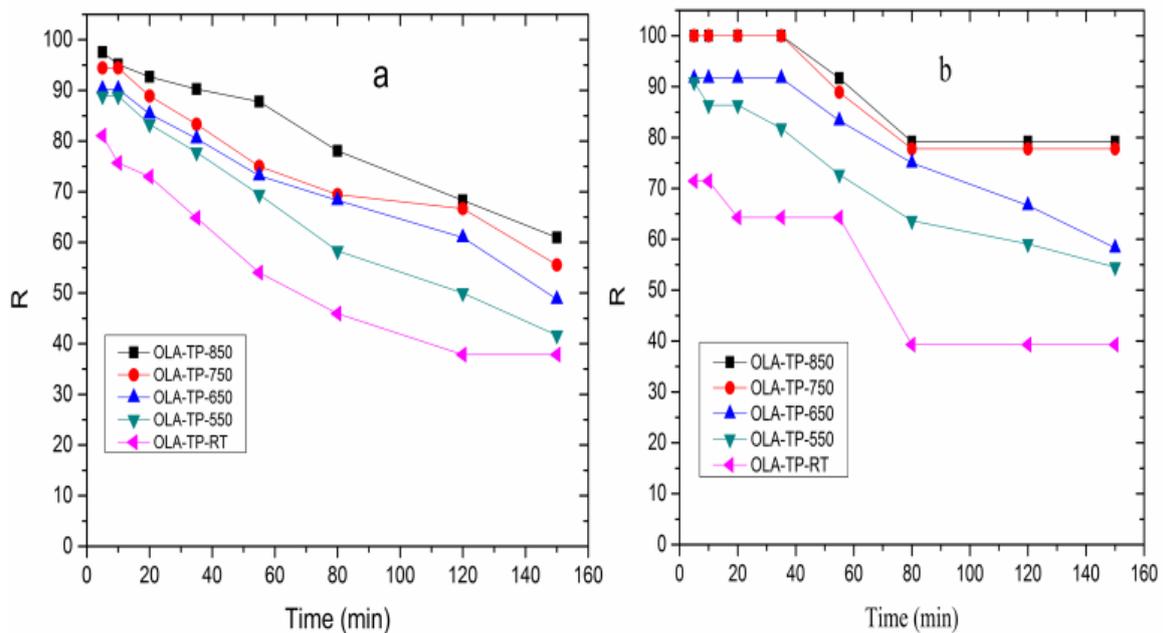


Figure 8: Effect of calcination temperature on removal efficiency of  $H_2S$  (a) and  $NH_3$  (b); OLA-TP samples, flowrate  $0.002$   $m^3/min$ , mass of the adsorbent 1 g.

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 m<sup>3</sup>/min. The values of the removal efficiency of H<sub>2</sub>S and NH<sub>3</sub> 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 m<sup>3</sup>/min the *R* values decrease from 71% to 20% for H<sub>2</sub>S and from 100% to 58% for NH<sub>3</sub>, respectively, measured after 150 min adsorbent's use.

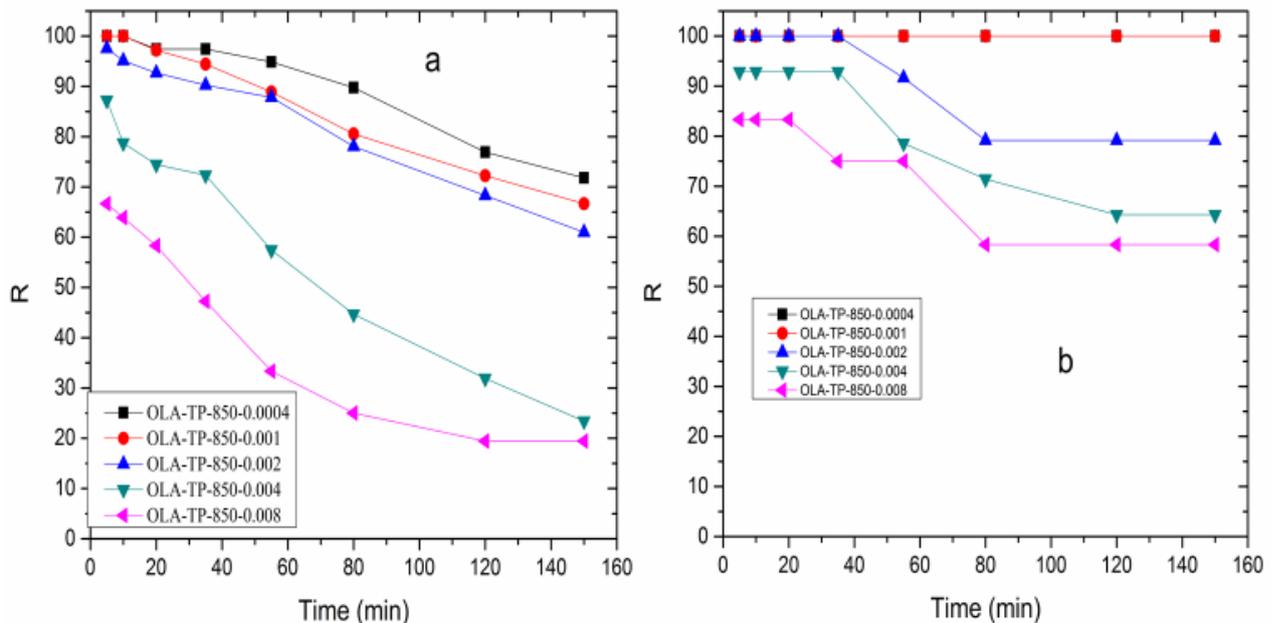


Figure 9: Effect of biogas flowrate on removal efficiency of H<sub>2</sub>S (a) and NH<sub>3</sub> (b); OLA-TP-850, mass of the adsorbent 1 g.

It seems at low flowrate (0.0004 m<sup>3</sup>/min) the materials get enough contact time for interaction between gas molecules and adsorbent; whereas at high flowrate (0.008 m<sup>3</sup>/min), H<sub>2</sub>S and NH<sub>3</sub> 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<sub>2</sub>S and NH<sub>3</sub>; 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<sub>2</sub>S and from 50% to 100% for NH<sub>3</sub> measured after 150 min adsorbent's use. When the mass of adsorbent was 2 g, the material retained 100% H<sub>2</sub>S removal after 40 min and efficiency decreased to 80% after 150 min; while for NH<sub>3</sub> the adsorbent held 100% removal efficiency for all time measurements.

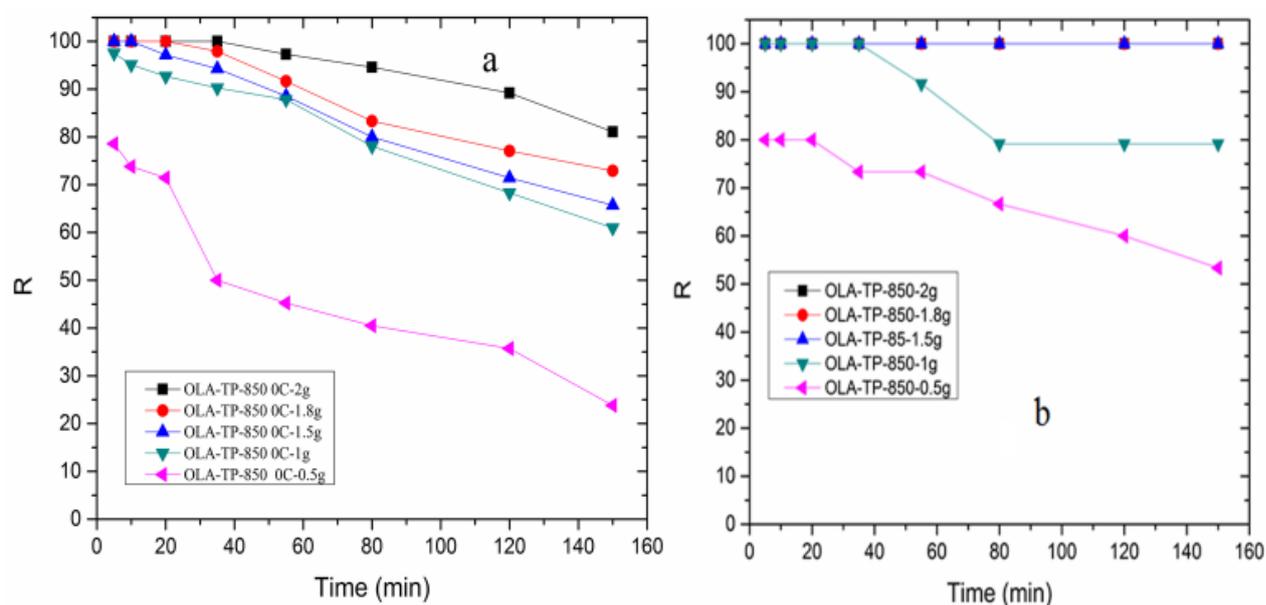


Figure 10: Effect of biogas flowrate on removal efficiency of H<sub>2</sub>S (a) and NH<sub>3</sub> (b); OLA-TP-850, mass of the adsorbent 1 g.

#### 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 <sup>3</sup> /min	H <sub>2</sub> S removal, g S/100 g of adsorbent	pH	Ref.
Moist soils	1–5	8.00×10 <sup>-5</sup>	0.50	5.70–7.70	(Bremner and Banwart, 1976)
Montmorillonite clay	12.50	51.00×10 <sup>-2</sup>	1.27	9.00	(Nguyen-Thanh <i>et al.</i> , 2005)
Municipal waste bottom ash	13×10 <sup>3</sup>	55.94×10 <sup>-3</sup>	0.30	9.80	(Ducom <i>et al.</i> , 2009)
Red mud soil	5	5×10 <sup>-5</sup>	2.10	> 13.00	(Sahu <i>et al.</i> , 2011)
Coal ashes	10	14.20×10 <sup>-5</sup>	0.50	11.90 ± 0.01	(Kastner <i>et al.</i> , 2002)
OLA-TP-850	1	2×10 <sup>-3</sup>	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 H<sub>2</sub>S 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 H<sub>2</sub>S and NH<sub>3</sub> 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 H<sub>2</sub>S and NH<sub>3</sub> 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 H<sub>2</sub>S and NH<sub>3</sub> 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 H<sub>2</sub>S and NH<sub>3</sub>. Moreover, chemisorption of H<sub>2</sub>S was confirmed via bornite (Cu<sub>5</sub>FeS<sub>4</sub>) and hexahydrite (MgSO<sub>4</sub>·6(H<sub>2</sub>O)) formation after sorption, while CO<sub>2</sub> and NH<sub>3</sub> removal was confirmed via trona Na<sub>3</sub>H(CO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>, pirssonite CaNa<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> and nahcolite NaHCO<sub>3</sub> formation.

#### 5.2 Recommendations

In my on-site experiment, the biogas flowrate and mass of adsorbent were variable parameters. The inlet concentration of H<sub>2</sub>S 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 H<sub>2</sub>S and NH<sub>3</sub> 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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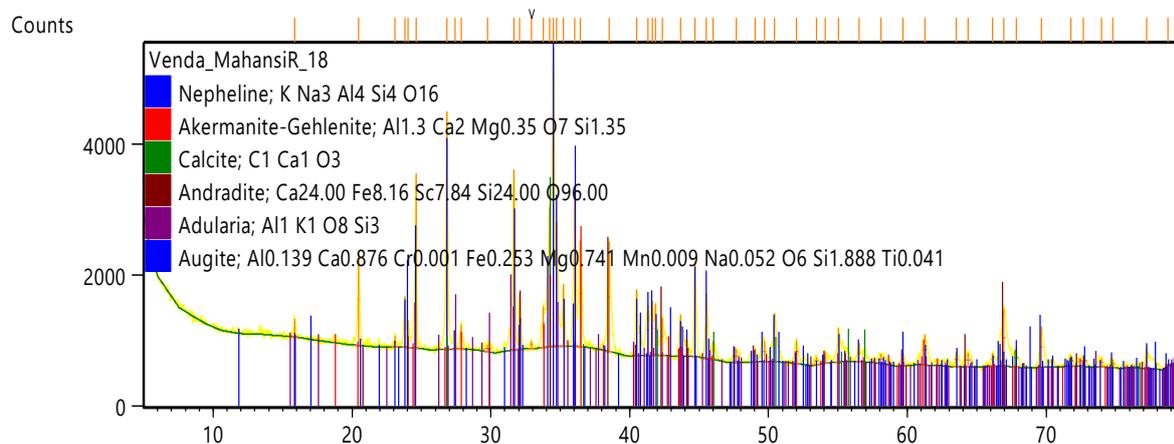
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## APPENDICES

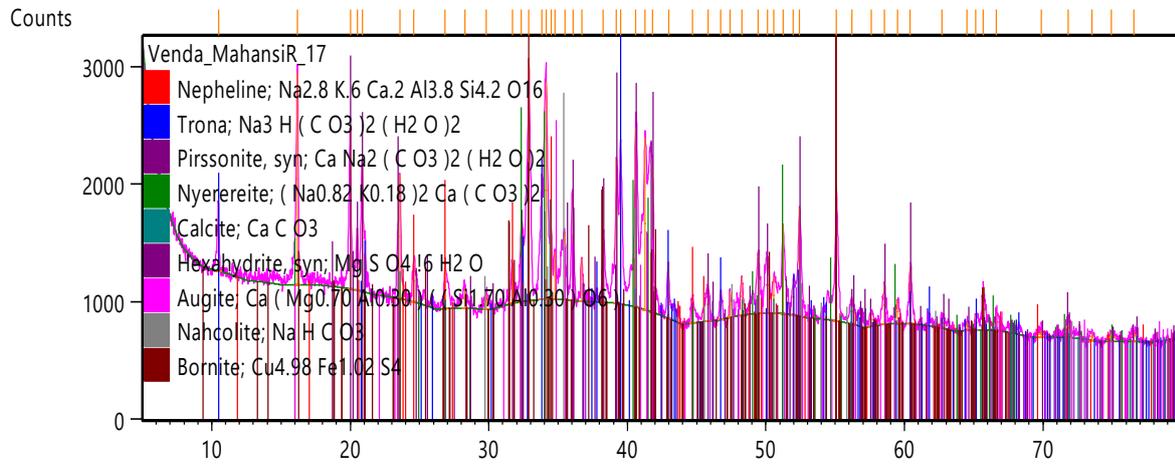
The analysis were performed at The University of Venda, Pretoria 002, South Africa.

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



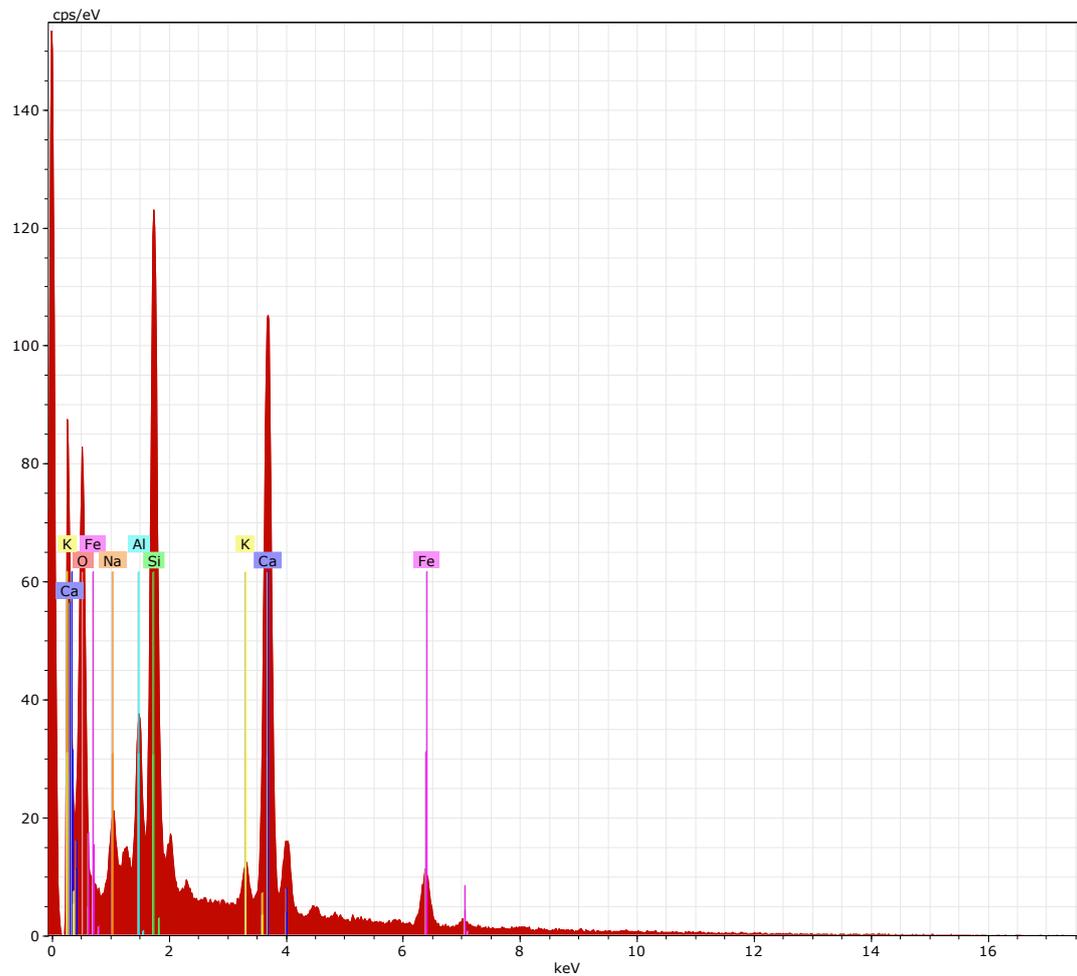
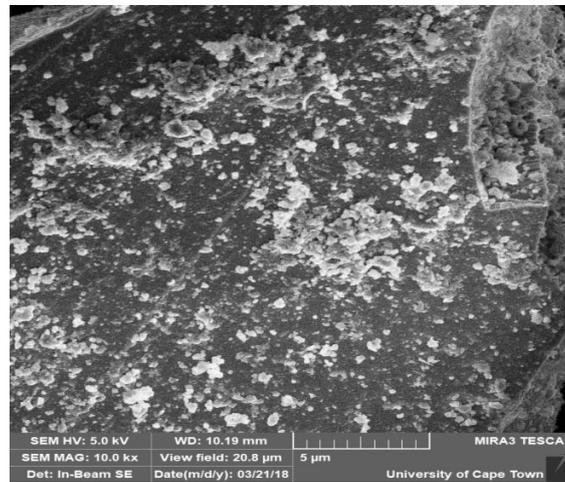
Peak List
Nepheline; K Na <sub>3</sub> Al <sub>4</sub> Si <sub>4</sub> O <sub>16</sub>
Akermanite-Gehlenite; Al <sub>1.3</sub> Ca <sub>2</sub> Mg <sub>0.35</sub> O <sub>7</sub> Si <sub>1.35</sub>
Calcite; C <sub>1</sub> Ca <sub>1</sub> O <sub>3</sub>
Andradite; Ca <sub>24.00</sub> Fe <sub>8.16</sub>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

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

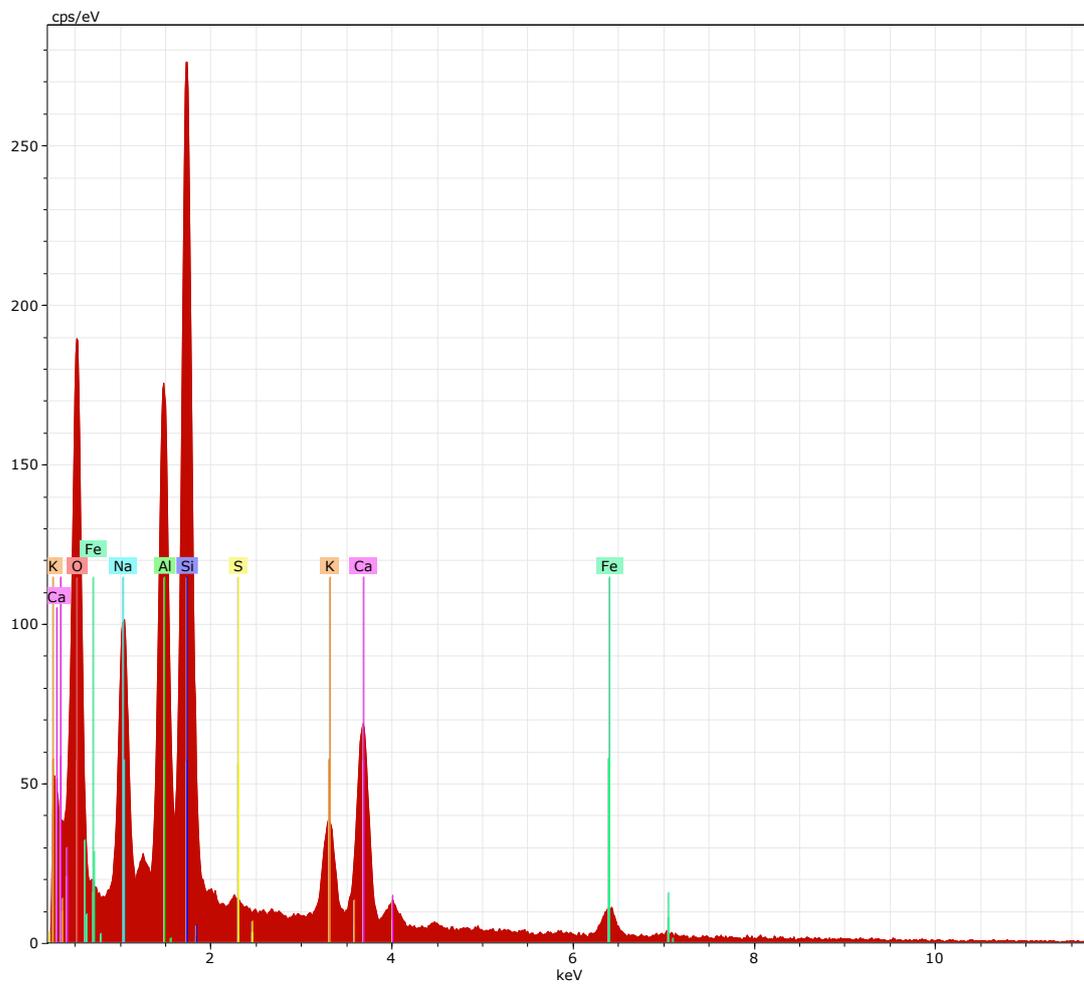
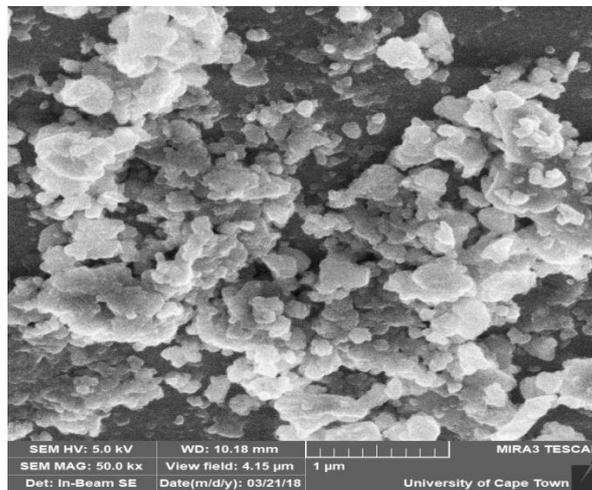


Peak List
Nepheline; Na <sub>2.8</sub> K <sub>0.6</sub> Ca <sub>2</sub> Al <sub>3.8</sub> Si <sub>4.2</sub> O <sub>16</sub>
Trona; Na <sub>3</sub> H (C O <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>
Pirssonite, syn; Ca Na <sub>2</sub> (C O <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O)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

**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 Pogrebnya, 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 H<sub>2</sub>S and NH<sub>3</sub> 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 H<sub>2</sub>S produces poisonous sulfur dioxide (SO<sub>2</sub>), which dissolves in engine oil causing the oil to become acidic and lose its ability to lubricate (Nicolas and Steve, 2009). Ammonia (NH<sub>3</sub>) in biogas stream when released free to the atmosphere, it endures a number of chemical reactions troubling the atmospheric equilibrium. Removal of H<sub>2</sub>S and NH<sub>3</sub> 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 H<sub>2</sub>S and NH<sub>3</sub> 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 H<sub>2</sub>S and NH<sub>3</sub>.
- 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

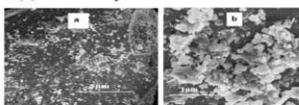


Figure 2: Surface morphology of OLA-TP-850 sample (a) before and (b) after adsorption.

- Figure 1 indicates the adsorption of H<sub>2</sub>S and CO<sub>2</sub> by formation of hexahydrite and trona.
- Figure 2 Indicate sample after adsorption the surface features showed crystalline white spherical particles that indicates considerable porosity which evidently provide efficient physisorption.
- Figure 3 and 4 indicate that sorption capacity increases with temperature raise
- OLA-TP-850 results in the SC of ~1.0 g S/100 g of adsorbent.

#### Methodology

Collection, drying and grinding of Oldoinyo Lengai Ashes

Calcination at temperature T<sub>c</sub> 550, 650, 750 and 850 °C

Adsorption of H<sub>2</sub>S and NH<sub>3</sub> from biogas using the OLA at Banana Investment Ltd Arusha

#### 2. Adsorption

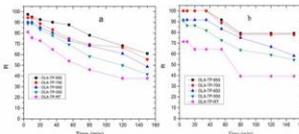


Figure 3: Effect of calcination temperature on removal efficiency of H<sub>2</sub>S (a) and NH<sub>3</sub> (b); OLA-TP samples, flowrate 0.002 m<sup>3</sup>/min, mass of the adsorbent 1 g.

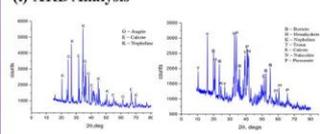
#### Conclusions

- The calcinated OLAs samples possess high adsorption efficiency of removing H<sub>2</sub>S and NH<sub>3</sub> from biogas.
- Chemisorption of H<sub>2</sub>S was confirmed via bornite (Cu<sub>5</sub>FeS<sub>4</sub>) and hexahydrite (MgSO<sub>4</sub> · 6H<sub>2</sub>O) formation after sorption, while CO<sub>2</sub> and NH<sub>3</sub> removal was confirmed via trona Na<sub>2</sub>H(CO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>, pirssonite CaNa<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> and nahcolite NaHCO<sub>3</sub> formation.

#### Results

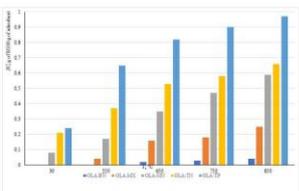
##### I. Characterization

(i) XRD Analysis



(a) (b)

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



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

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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 (H<sub>2</sub>S) and ammonia (NH<sub>3</sub>) 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 H<sub>2</sub>S and NH<sub>3</sub> 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 H<sub>2</sub>S and NH<sub>3</sub> 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, H<sub>2</sub>S and NH<sub>3</sub> 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 CH<sub>4</sub> and CO<sub>2</sub> 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 H<sub>2</sub>S 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<sub>α</sub> radiation source in a 2θ range between 10° and 80° at a scanning rate of 2° min<sup>-1</sup> 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 H<sub>2</sub>S and NH<sub>3</sub> Removal and Evaluation of Sorption Capacity of Adsorbents

The sorption experiment of H<sub>2</sub>S and NH<sub>3</sub> 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 m<sup>3</sup> daily, the composition of the gas was determined with the biogas 5000 g as analyzer to be 82% - 89% CH<sub>4</sub>, 12% - 15% CO<sub>2</sub>, <1% O<sub>2</sub>, 5 - 48 ppm of NH<sub>3</sub>, and 24 - 60 ppm of H<sub>2</sub>S [42].

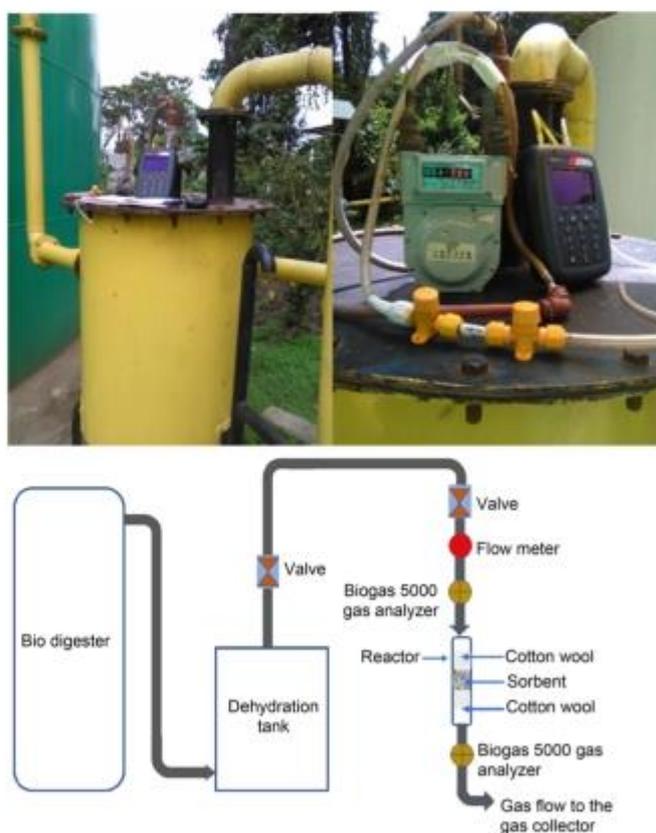
A reactor made of plastic tube, 6.5 cm length, 1.7 cm diameter, filled with adsorbent supported by cotton wool on both end sides of the reactor tube. The biogas allowed to flow through the reactor at ambient temperature varying the flowrate from 0.0004 to 0.008 m<sup>3</sup>/min, and mass of adsorbents from 0.5 to 2.0 g.

The mass of adsorbent of 1 g and the biogas flowrate of 0.002 m<sup>3</sup>/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 H<sub>2</sub>S and NH<sub>3</sub> 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 H<sub>2</sub>S and NH<sub>3</sub> 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].

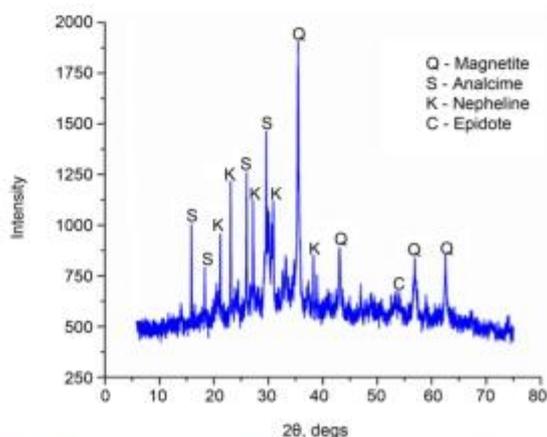
### 3.2. XRD Analysis of Calcinated OLA Samples

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  $49^\circ$  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.

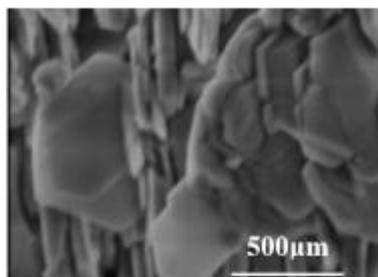
Apparently, the distinction of our results with literature [19] may be attributed to the different mineralogical and chemical composition of the adsorbents.

### 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

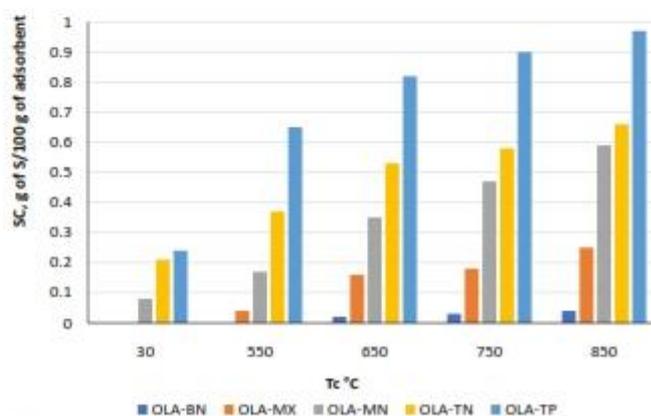
#### 3.4.1. Effect of Calcination Temperature and Height the Samples Were Collected

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.

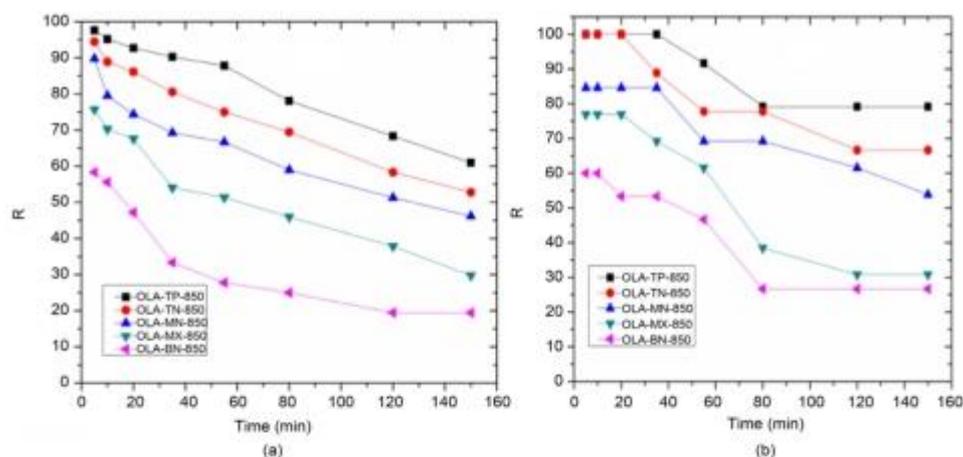
The adsorption efficiency removal  $R$  was measured both for  $H_2S$  and  $NH_3$  and analyzed for different samples with respect to time interval between the measurements of initial and final concentrations of the adsorbates while biogas flowed through the reactor. The plots for  $R$  vs time for 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 H<sub>2</sub>S removal: sorption capacity and breakthrough time; mass of adsorbent 1 g and the biogas flowrate 0.002 m<sup>3</sup>/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 m<sup>3</sup>/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  $1 \text{ g}$ .

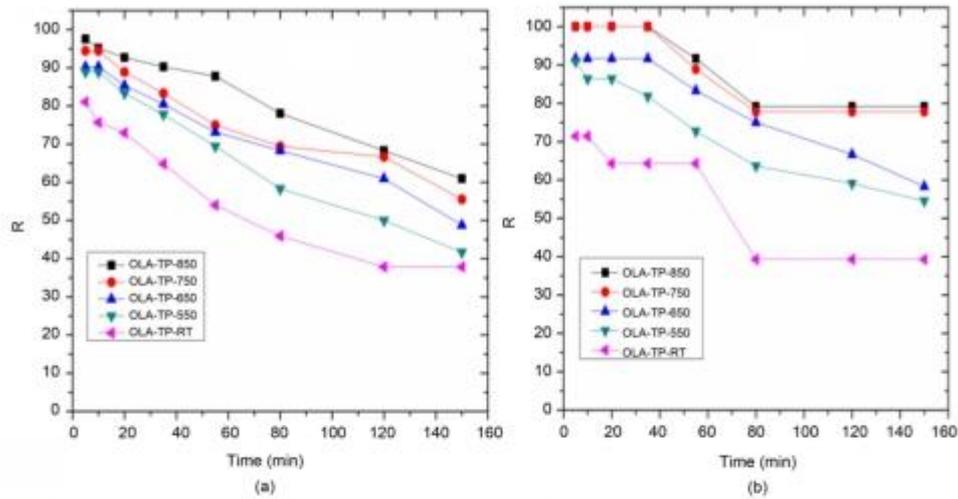
Similar trend is observed in **Figure 6** where the plots of  $R$  vs time are given for OLA-TP samples calcinated at different temperatures. The removal efficiency is increased with calcination temperature raise. Thus after 150 min of the adsorbent's use, the  $R$  of OLA-TP-RT descends to 37%, while 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  $R$ .

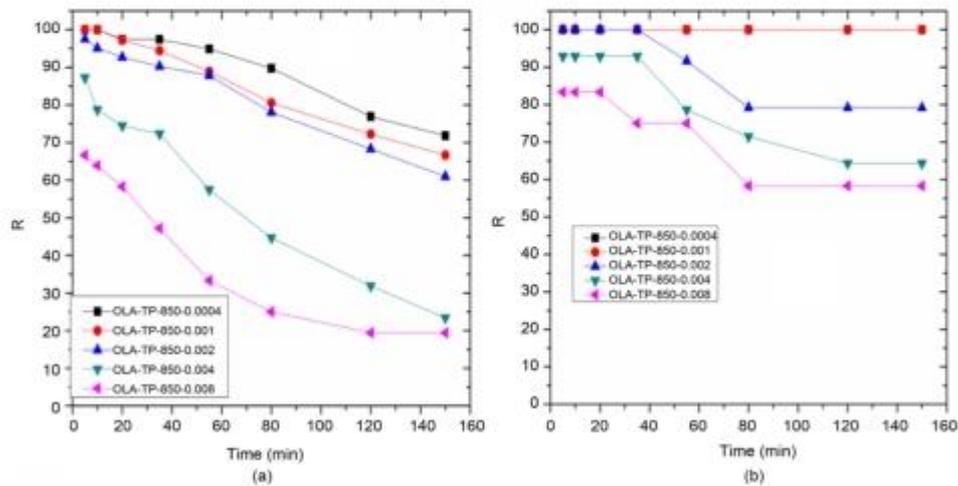
Therefore, among all OLA samples considered the ashes collected at the top site and calcinated at  $850^\circ C$ , the OLA-TP-850, demonstrated the best removal efficiency retaining it high during the exploitation time of the adsorbent.

### 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).

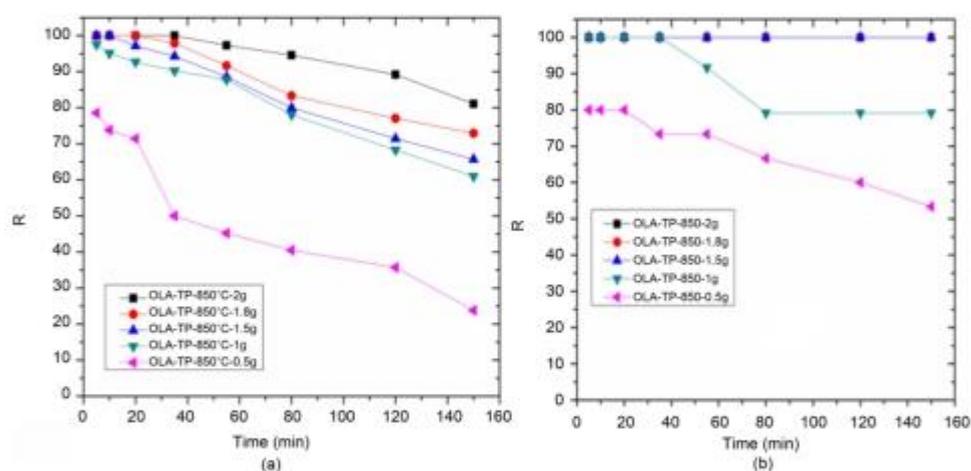


Figure 8. Effect of adsorbent mass on removal efficiency of  $H_2S$  (a) and  $NH_3$  (b); OLA-TP-850, flowrate  $0.002 \text{ m}^3/\text{min}$ .

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

Adsorbent	Mass, g	Biogas flowrate, $\text{m}^3/\text{min}$	$H_2S$ removal, g S/100g of adsorbent	pH	Ref.
Moist soils	1 - 5	$8.00 \times 10^{-4}$	0.50	5.70 - 7.70	[54]
Montmorillonite clay	12.50	$51.00 \times 10^{-2}$	1.27	9.00	[33]
Municipal waste bottom ash	$13 \times 10^4$	$55.94 \times 10^{-3}$	0.30	9.80	[55]
Red mud soil	5	$5 \times 10^{-1}$	2.10	>13.00	[19]
Coal ashes	10	$14.20 \times 10^{-3}$	0.50	$11.90 \pm 0.01$	[15]
OLA-TP-850	1	$2 \times 10^{-1}$	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 H<sub>2</sub>S 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 H<sub>2</sub>S and NH<sub>3</sub> 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 H<sub>2</sub>S and NH<sub>3</sub>. Moreover, chemisorption of H<sub>2</sub>S 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 H<sub>2</sub>S in biogas was controlled but difficult to keep constant. For the next step, it may be recommended to evaluate the effect of concentration of H<sub>2</sub>S and NH<sub>3</sub> 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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