

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

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How to cite this paper: Kandola, I., Pogrebnoi, A. and Pogrebnyaya, T. (2018) Oldoinyo Lengai Volcanic Ash for Removal of Hydrogen Sulfide and Ammonia from Biogas. *Journal of Materials Science and Chemical Engineering*, 6, 78-93.
<https://doi.org/10.4236/msce.2018.64010>

Received: February 19, 2018

Accepted: April 10, 2018

Published: April 13, 2018

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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_2S) and ammonia (NH_3) from biogas was investigated. The samples were calcinated at different temperatures ($550^\circ C$ - $850^\circ C$) 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_2S and NH_3 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_2S and NH_3 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 $850^\circ C$ exhibited the best sorption performance.

Keywords

Adsorption, Calcination, Flowrate, Oldoinyo Lengai, Volcanic Ash, H_2S and NH_3 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_4 and CO_2 which are the main constituents, but also contains in-

sufficient amount of contaminants such as H₂S, NH₃, 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 H₂S 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 H₂S from biogas stream prior to use.

Researchers 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 [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 H₂S 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], Penausende muscovite [31], laterite [32], montmorillonite [33] [34], which are economically feasible for CO₂ and H₂S 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 H₂S and NH₃ 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 H₂S and NH₃ 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 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.

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 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 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];

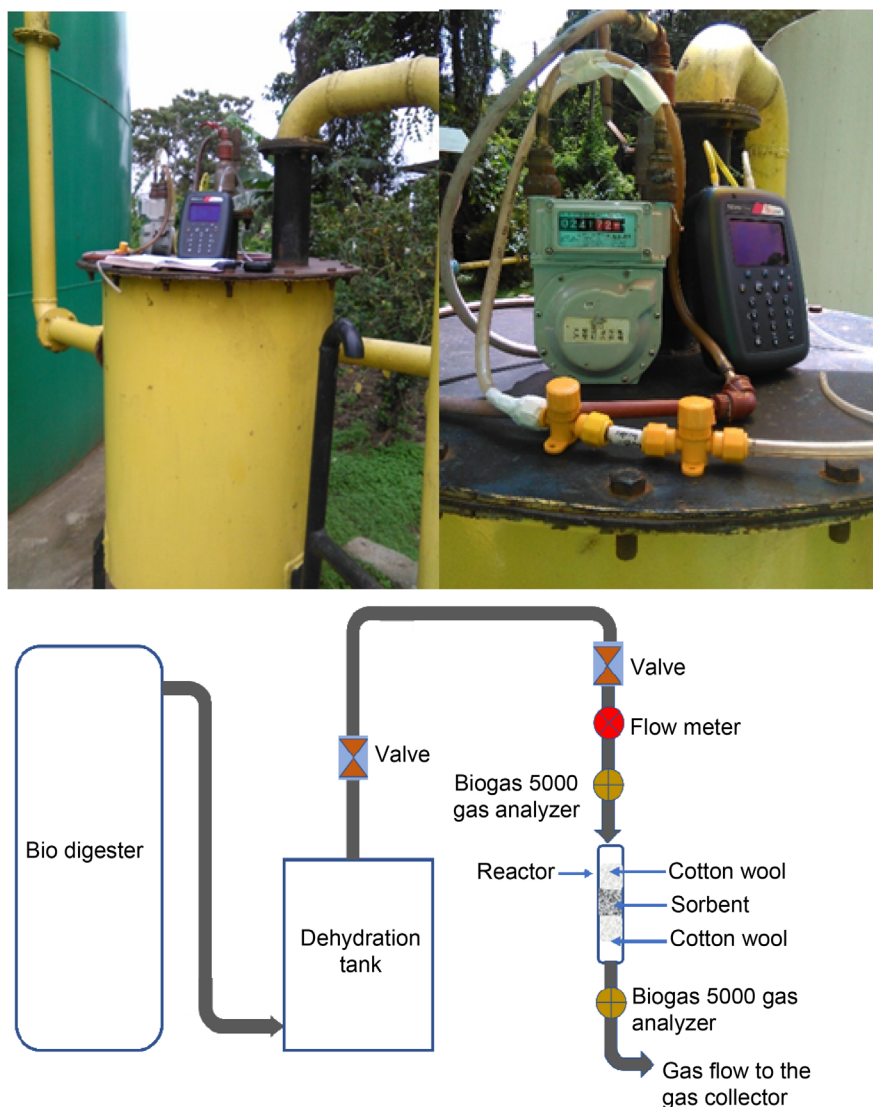


Figure 1. Photos and schematic diagram of the sorption experimental setup.

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

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 H₂S 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 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 [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 Na₃H(SO₄)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 H₂S removal, and after sorption FeS₂, FeS, CaSO₄·2H₂O, 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

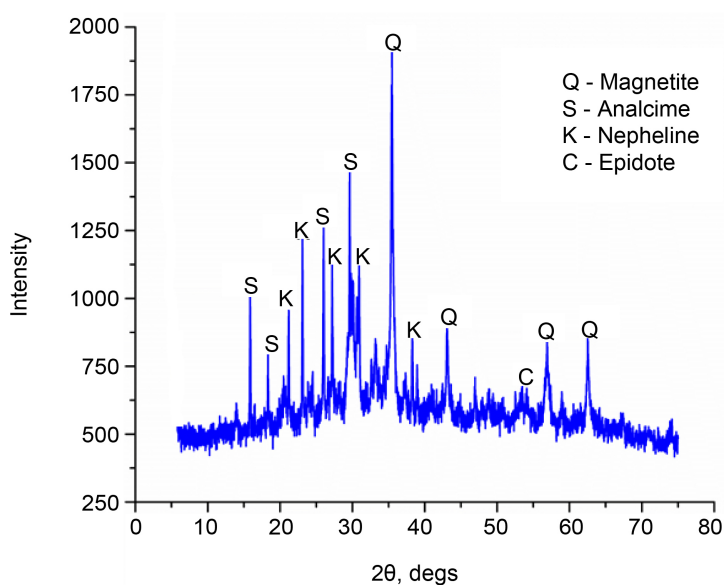


Figure 2. XRD patterns for OLA-TP-850 sample before adsorption.

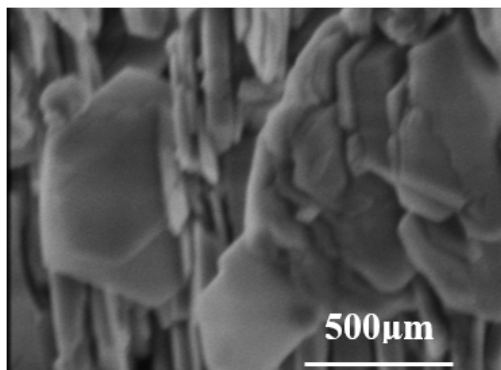


Figure 3. Surface morphology of OLA-TP-850 sample before adsorption.

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 $\sim 10\%$ 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

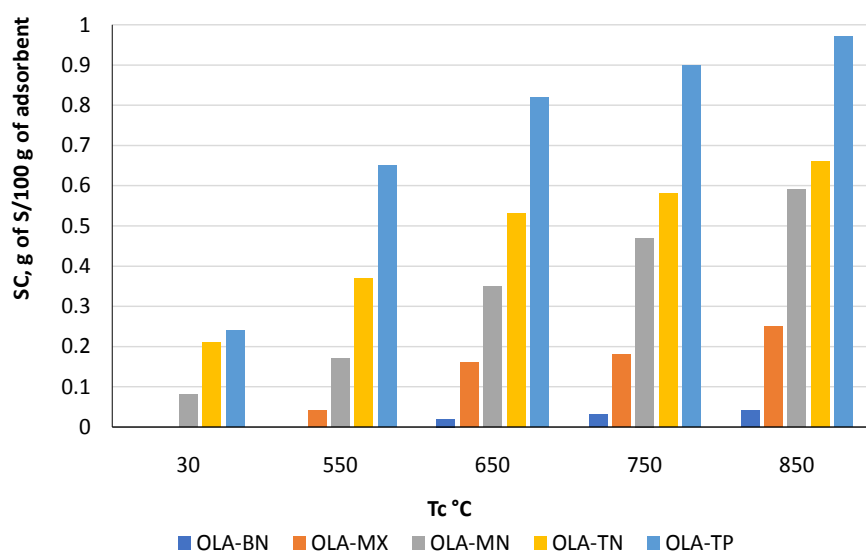


Figure 4. Sorption capacity of Oldoinyo Lengai ash materials for hydrogen sulfide removal; mass of adsorbent 1 g and the biogas flowrate 0.002 m³/min.

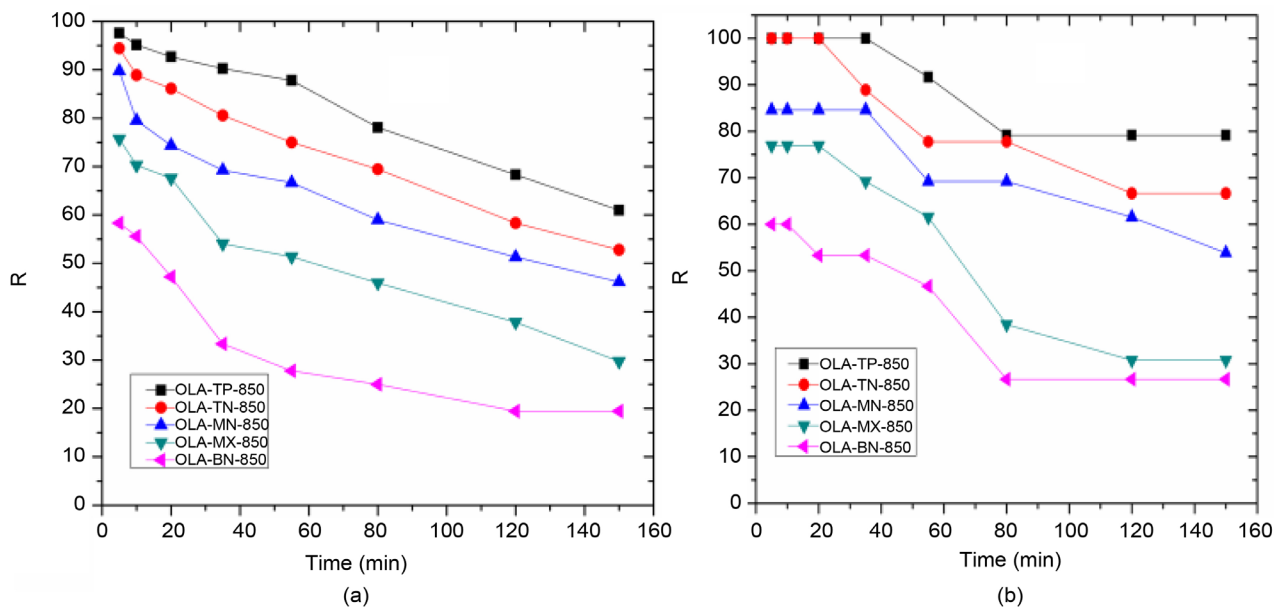


Figure 5. Effect of the site location on the removal efficiency of H₂S (a) and NH₃ (b); for all samples $T_c = 850^\circ\text{C}$, flowrate 0.002 m³/min, mass of the adsorbent 1 g.

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 descents to 37%, while the OLA-TP-850 holds 60% for H₂S 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 H₂S and NH₃, 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 NH₃ per 1 g of the biogas, that is one order less than of H₂S) 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°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 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 7**. One can see, with the flowrate raise from 0.0004

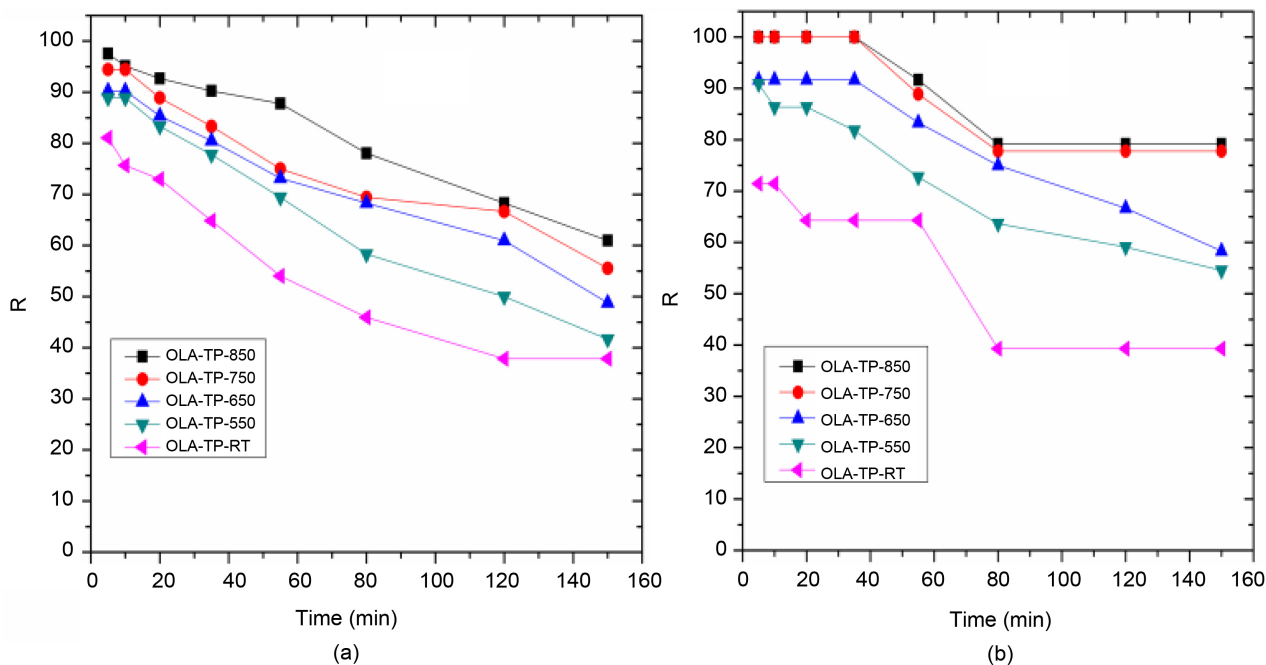


Figure 6. Effect of calcination temperature on removal efficiency of H₂S (a) and NH₃ (b); OLA-TP samples, flowrate 0.002 m³/min, mass of the adsorbent 1 g.

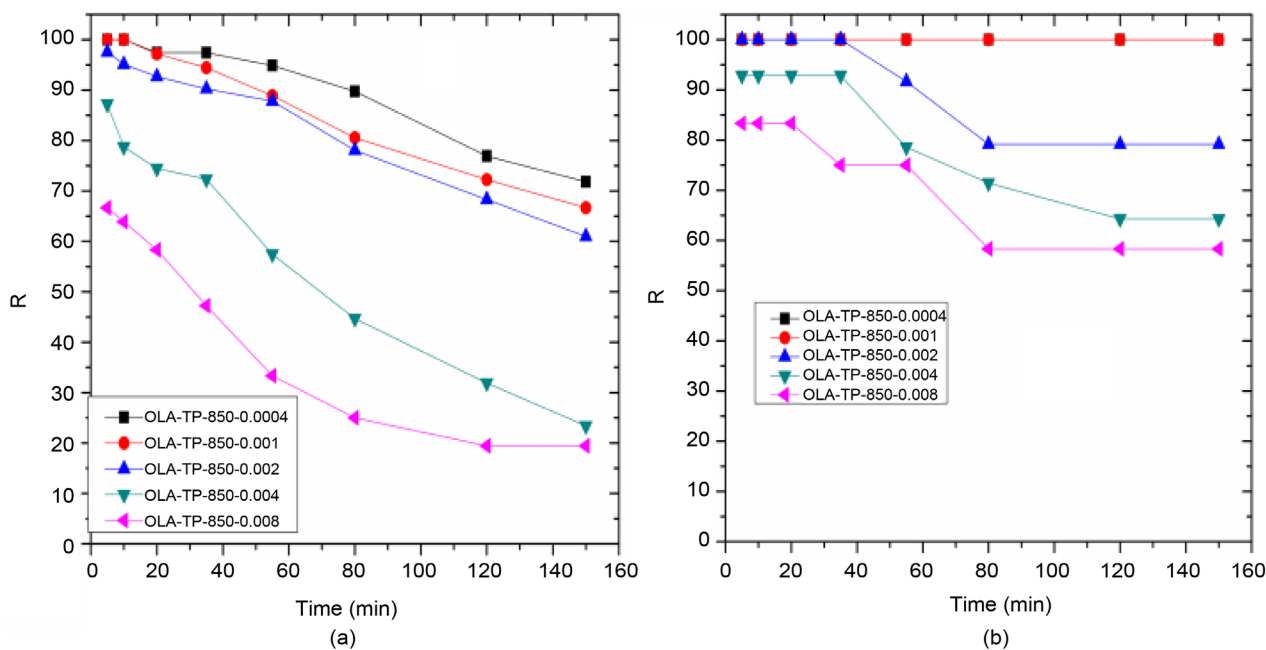


Figure 7. Effect of biogas flowrate on removal efficiency of H₂S (a) and NH₃ (b); OLA-TP-850, mass of the adsorbent 1 g.

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.

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 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).

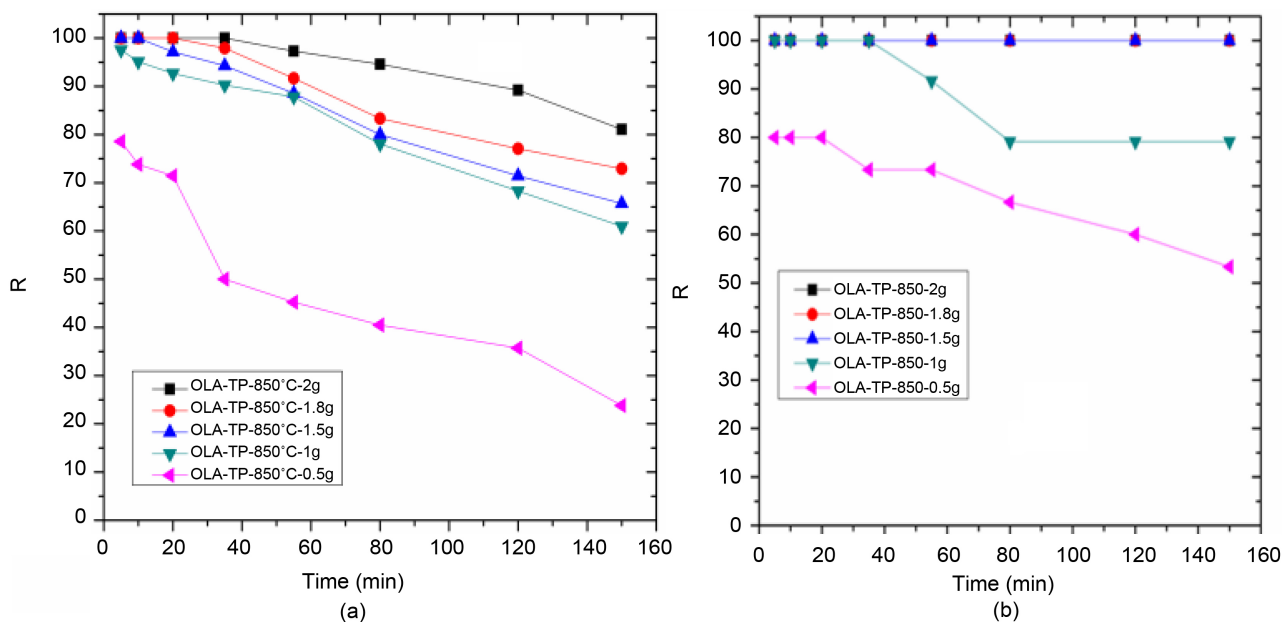


Figure 8. Effect of adsorbent mass on removal efficiency of H_2S (a) and NH_3 (b); OLA-TP-850, flowrate $0.002 \text{ m}^3/\text{min}$.

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^{-5}	0.50	5.70 - 7.70	[54]
Montmorillonite clay	12.50	51.00×10^{-2}	1.27	9.00	[33]
Municipal waste bottom ash	13×10^3	55.94×10^{-3}	0.30	9.80	[55]
Red mud soil	5	5×10^{-5}	2.10	>13.00	[19]
Coal ashes	10	14.20×10^{-5}	0.50	11.90 ± 0.01	[15]
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.

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.

Acknowledgements

The authors thank the German Academic Exchange Service DAAD, for the award of the scholarship which catered for paying tuition fees and accommodation to undertake the MSc studies at The Nelson Mandela African Institution of Science and Technology. Prof. K. Njau through VLIR-IUC/NM-AIST partnership programme is highly acknowledged for the financial support and Department of Materials Science and Engineering, University of Connecticut, USA, for scanning electron microscope (SEM) analysis allowed to render this study.

Conflict of Interest

The authors have not declared any conflict of interest.

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