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Research Article

Removal of Hydrogen Sulfide from Biogas Using a Red Rock

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The potential of red rock (RR) materials for the removal of H_2S from biogas was studied. The rock samples were collected, sieved, and organized in various particle size ranges such as $0.32\text{-}250\ \mu\text{m}$, $250\text{-}500\ \mu\text{m}$, $500\text{-}750\ \mu\text{m}$, $750\ \mu\text{m}\text{-}1\ \text{mm}$, and $1\text{-}1.5\ \text{mm}$. These samples were calcinated at the various temperatures as 500°C , 750°C , and 1000°C and then characterized for phase composition by energy-dispersive X-ray florescent technique, surface morphology by Zeiss Ultra Plus Field Emission Scanning Electron Microscopy (FE-SEM), and surface area by the Brunauer-Emmett-Teller (BET) method. The calcinated RR was filled in the bed reactor, and biogas was allowed to pass through the adsorbent while recording the inlet and exit concentration of H_2S . The results show that particle size, calcination temperature, adsorbent mass, and biogas flow rate were parameters that influenced the removal efficiency and adsorption capacity of RR. The sample sieved at $0.32\text{-}250\ \mu\text{m}$ and calcinated at a temperature of 1000°C showed 95% high removal efficiency and adsorption capacity of $0.37\ \text{g}/100\ \text{g}$ of the sorbent. Regeneration of spent materials when exposed to air, keep on by reuse in the column, appeared to have nearly similar removal efficiency as the original calcined sample. Thus, the overall performance of the material is promising, which is due to the presence of metals such as iron and magnesium, among others. Therefore, proving the successful elimination of contaminant, RR is an available material for biogas purification.

1. Introduction

Biogas is a mixture of various gasses that are obtained through the biological degradation of organic matter in the lack of oxygen [1]. It is a renewable energy that belongs to the category of biofuels. The biogas composition differs according to the material used in the whole process of production. The main components are carbon dioxide (CO_2) and methane (CH_4), although it likewise encompasses some amounts of contaminants like H_2S , NH_3 , volatile halogenated organics, and siloxanes [2].

Kitchen waste, bagasse, and garden waste can be used to produce biogas. These wastes from food remains, bagasse, and garden waste are naturally organic, hence easily degradable by a microorganism [3] which then release ammonia gas, carbon dioxide, methane, and hydrogen sulfide to the atmosphere. Compositions are carbon dioxide 30-45%, methane 50-70%, and some impurities like hydrogen sulfide [4]. Therefore, to make the environment clean, these wastes can be used to produce biogas. The recommended industrial

exposure limit for H_2S is from 8-10 ppm per day [5], and according to WHO, it is 0.05 mg/L [6].

The availability of hydrogen sulfide in ignition process leads to the formation of SO_2 which is very detrimental to the ecosystem [7, 8] and harmful for animal health and human as it leads to headaches, nausea, dizziness, irritation of mucous membranes, and sudden death. Therefore, care has to be taken to remove hydrogen sulfide before biogas is used. The current researchers are mostly searching for materials that could cause the elimination of H_2S from biogas. Several materials can adsorb and take hydrogen sulfide from biogas [2, 9-11]. There are various methods used in removing H_2S from biogas and commonly can be classified into two major groups as physical-chemical approaches and biotechnological method, the former one being traditional but dominates the today's market [12]. The biological method used in the purification of biogas is biotrickling filters, biofilters, and bioscrubbers [13]. In physical adsorption, gas molecule attracts and adheres to the surface of adsorbent by using intermolecular forces and this process

is ordinarily exothermic, the heat that is released ranging from 2 to 20 kJ/g·mol [14]. Chemical sorption is a process that involves the reaction between the surface of the material and the adsorbent where there is a creation of a new chemical bond at the surface of the adsorbent as surface chemistry and surface area plays an essential part for hydrogen sulfide elimination [15].

Red soil is a remaining product of an intensive chemical weathering process that affects rocks through leaching and oxidizing processes. Literature shows that red soils contain a massive amount of iron in the form of magnetite (Fe_3O_4), goethite [$\text{FeO}(\text{OH})$], and hematite (Fe_2O_3) [16]. Biogas adsorption is a prominent method due to low-cost material as red mud soil and clay soil [17, 18] which are rich in iron oxide where H_2S will be oxidized by iron oxide into elemental sulfur.

By considering the benefits of biogas, there is a need of developing cost-effective materials for the purification process [19]. Therefore, this study is intended at investigating the elimination of hydrogen sulfide from biogas using RR materials collected from Nadosoito village in Monduli district in Tanzania. The red color of the materials makes them peculiar and unique, indicating possible iron presence which might facilitate the hydrogen sulfide removal and thus would be worth for investigation. The biogas purification process was done on-site at ambient conditions.

2. Materials and Methods

2.1. Sample Collection and Adsorbent Preparation. RR materials were collected from Nadosoito village in Monduli district, which is located in the Northern part of Tanzania -3.42703 South and 36.44103 East. This material contains Na, Mg, K, Ca, Zn, and Fe in high proportions. The material was crushed, sieved into diverse particle size as 0.32-250 μm , 250-500 μm , 500-750 μm , 750 μm -1 mm, and 1-1.5 mm, and then samples were calcinated at various temperatures as 500°C, 750°C, and 1000°C for about 2 hours in the furnace (Thermo Scientific 1200 Box Furnace) and then permissible to cool ready for adsorption purposes.

2.2. Material Characterization. The textural properties of the red rock samples were analyzed; the specific surface area was determined by the Brunauer-Emmett-Teller (BET) method while pore size distribution evaluated through the Barrett-Joyner-Halenda (BJH) method. Nitrogen adsorption-desorption isotherms were evaluated at 77 K by using the Quantachrome NOVA 4200 (Win©1994-2013, v11.03) at University of Dar es Salaam. The BET surface area, pore diameter, and pore volume were analyzed for the raw sample, calcined, and those that had undergone adsorption. Sample composition was determined by energy-dispersive X-ray fluorescence spectrometer (XRF), model MiniPal4 (Pw4030)-Rh manufactured by PAN Analytical, using the software provided with the instrument. The surface morphology of the samples (RR-B) and (RR-C) was investigated using Zeiss Ultra Plus Field Emission Scanning Electron Microscopy (FE-SEM) from Indian Institute of Science and Technology Bangalore.

2.3. Evaluation of Adsorbent Performance. The sorption and removal experiments were carried out at domestic household premises in Arusha, Tanzania, where the biogas was produced in two digesters from biomass, human wastes, and the kitchen remaining wastes. A plastic bed reactor of 5 cm length and 1 cm width was packed with cotton wool inside, and without the adsorbent, biogas was allowed to pass through the reactor at the ambient condition to verify whether cotton wool does absorb H_2S or not; it appeared that cotton wool does not react with H_2S . The adsorbent was filled in the bed reactor where both ends of the bed reactor were supported with cotton wool, and the biogas was then allowed to pass through. The concentration of H_2S was measured once before the filter and then monitored every 10 minutes after the filter.

Photo and schematic diagram for the experimental setup are shown in Figure 1. Flowmeter model JBD2.5-SA was used to monitor the flow rate, while for measuring the gases found in the biogas, the Geotech Biogas 5000 analyzer model was used.

The adsorbent performance was expressed as percentage removal efficiency (RE), and it was calculated by using the formula below:

$$\text{RE} = \frac{C_0 - C}{C_0} 100\% \quad (1)$$

Sorption capacity (SC) of the RR samples, in a gram of sulfur per 100 grams of sorbent, was determined as defined in the literature [20]:

$$\text{SC} = \text{WHSV} \frac{M}{V_{\text{mol}}} \int_0^t \frac{\partial C_0}{\partial C} C \partial t, \quad (2)$$

where M is the atomic weight of sulfur, WHSV is the weight hourly space velocity in $\text{mLh}^{-1}\text{g}^{-1}$, V_{mol} is the gas molar volume at standard conditions in Lmol^{-1} , C_0 and C are the concentrations of H_2S before and after adsorption, respectively, in ppm, and t is operating time [20].

2.4. Sample Regeneration. A separate experiment was done to examine the capability to regenerate an adsorbent by exposure to air. Experiment on the removal of H_2S was first performed on RR samples for about 150 min, following this test; the sample was removed from the bed reactor and spread in a sheet to exposure to air over one week. The sample was filled back into the bed reactor, and the experiment on the H_2S removal test was proceeded.

3. Results and Discussion

3.1. Composition of Biogas. On-site experiment for determining biogas composition was carried out using Biogas 5000 gas analyzer as per Table 1. The biogas composition in two digesters differs according to feedstock used and the size of the digester.

Hydrogen sulfide concentration was monitored for about one hour before the adsorption process. In digester one, the

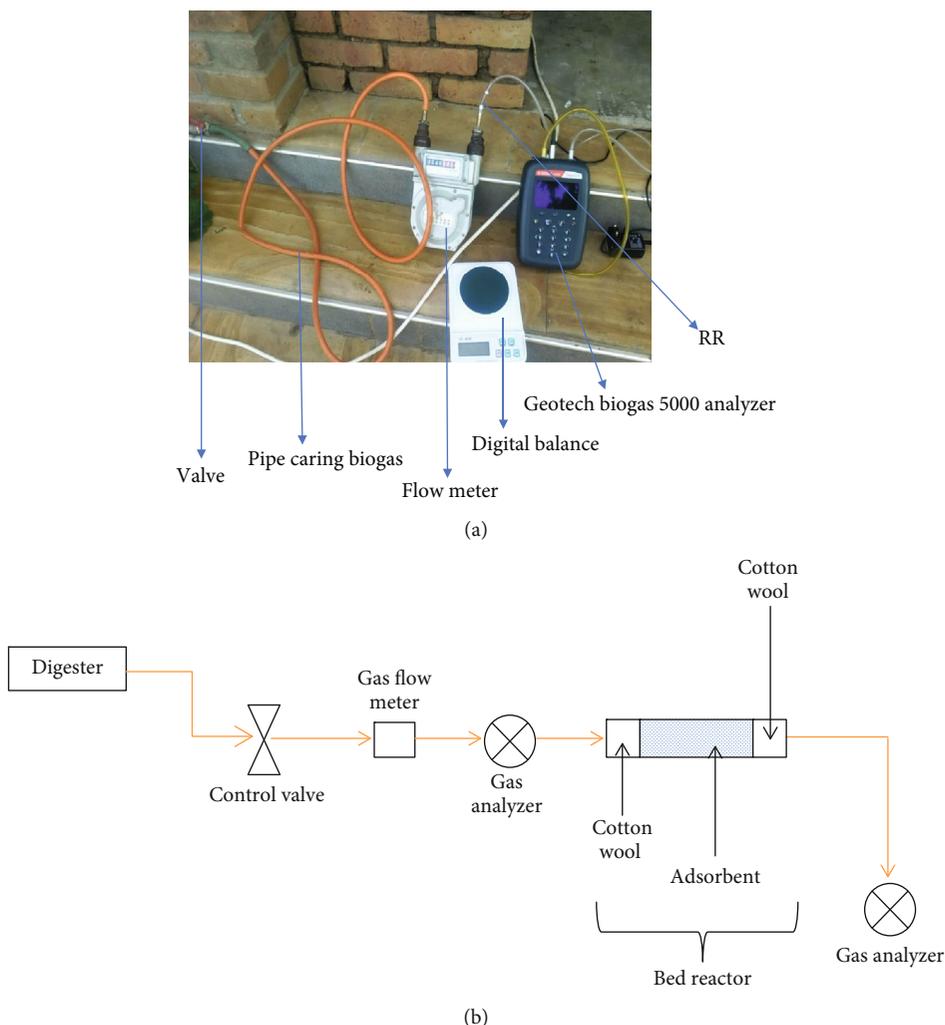


FIGURE 1: On-site experiment of biogas purification: photo (a) and schematic diagram (b).

TABLE 1: Composition of biogas within two digesters.

Component	Biogas in digester 1	Biogas in digester 2
CH ₄	65-69%	70-71%
CO ₂	34-37%	27-29%
H ₂ S	526-539 ppm	801-1230 ppm
NH ₃	18-20 ppm	20-24 ppm

H₂S concentration remains nearly constant while in digester two it varies because of the feedstock variation.

3.2. Textural Characteristics of the Adsorbent. The textural properties of the RR materials have been analysed for three samples, raw sample RR-A, calcined sample at $T_c = 1000^\circ\text{C}$ RR-B, and the sample has undergone adsorption RR-C. Nitrogen adsorption/desorption isotherms are displayed in Figure 2(a), while Figure 2(b) displays pore size distribution, calculated through the BJH method.

Consider Figure 2(a); the calcined sample RR-B adsorbs more N₂ compared to the rest as it poses the highest BET surface area as per Table 2.

In Figure 2(b), is seen, the sample RR-B possesses large pore diameter; hence, it has more differential volume when compared to other samples, and it is following a large surface area.

The BET analysis summary is displayed in Table 2 for three samples: as it is seen, the BET surface area of the raw sample RR-A is smaller compared to the calcined sample RR-B while eventually decreases in the sample RR-C that undergoes adsorption because the micropores created had occupied by adsorbate. The pore size evaluation of all samples shows they are of more mesopores rather than macropores. Availability of micropores and mesopores should favor adsorption as reported in the literature [21].

3.3. Morphological Studies. The surface morphology of calcined (RR-B) and utilized sample (RR-C) is as shown in SEM image in (Figure 3). The morphology of calcined sample (Figure 3(a)) and (Figure 3(c)) showed there was small but irregular pore size with roughness on surface due to calcination effect as the result surface area increased which reflects Table 2 above. Worth to note that morphology of RR is very similar to that observed by [22] where red mud was used for

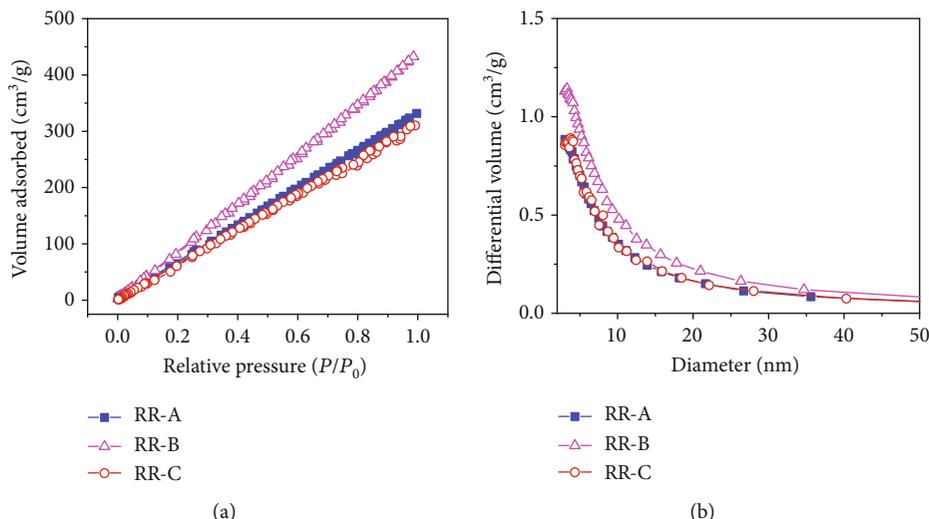


FIGURE 2: (a) Nitrogen adsorption/desorption isotherms. (b) Pore size distribution calculated from desorption isotherm using the BJH method.

TABLE 2: Multipoint BET summary for raw sample (RR-A), calcined (RR-B), and utilized sample (RR-C).

Sample	Particle size (μm)	$S_{(\text{BET})}$ (m^2/g)	Pore diameter (\AA)	$V_{(\text{total})}$ (cc/g)	Ref
RR-A	0.32-250	546	31	0.47	This study
RR-B	0.32-250	696	32	0.63	This study
RR-C	0.32-250	494	30	0.48	This study
Red mud	0.1-160	31.7	18.2	0.015	[22]

hydrogen sulfide adsorption. Nevertheless, spent sample (RR-C) pores collapse and formation of spots and channelled like structure was observed which might be due to the hydrogen sulfide attachment (Figure 3(b)) and (Figure 3(d)). Therefore, according to this surface morphology, it supports Table 2 that means the spent sample decreases in surface area due to the attachment of hydrogen sulfide.

3.4. Mineral Composition and pH of RR Material. Elemental composition of RR material calcined at 1000°C is displayed via bar diagram in Figure 4 whereby the results from XRF analysis show that Si, Ca, Fe, and Al are most abundant compounds present in the sample. Some transition elements also were found but in a minimal amount. The pH value for the red rock sample falls under basic, which is about 10. The alkalinity of the red rock favors the hydrogen sulfide removal. This phenomenon is similar to the observation reported in [23]. The oxides of some elements are available in the RR (Table 3, and the iron oxide is present in a higher amount compared to other elements that favour facilitating the whole process of purification. According to literature, two forms of iron oxide have excellent removal efficiency of hydrogen sulfide from biogas that is $\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$. They react very rapidly with hydrogen sulfide, and the regeneration process is practically completed [24]. In addition to iron(III) oxide, the following metal oxides may be detected: aluminium, sodium, magnesium, titanium, calcium, and potassium; although the oxides of the mentioned metal exhibit very minimal hydrogen sulfide reaction at room temperature, instead they react

with carbon dioxide found in biogas and in air [24]. Bauxite $\text{Al}(\text{OH})_3$ has been used for biogas purification with a removal efficiency of 94.7%, although it contains silica, some clay minerals, iron hydroxide, and different oxides of which only bauxite reacts with hydrogen sulfide from biogas [25]. Additionally, activated MgO has been used for purification of biogas, especially carbon dioxide removal [26] and not hydrogen sulfide. Activated carbon and iron sponge can be used to remove H_2S from biogas; CO_2 is removed using amine solution, sodium hydroxide, and potassium hydroxide [19, 27] while water is removed through the use of silica gel [28, 29]. This supports the current study that iron oxide is mostly responsible for the removal of H_2S from biogas rather than oxides of the elements found in the sample RR.

3.5. Adsorption Ability of RR Material. In this section, adsorption performance of the RRs was explored in terms of the effect of particle size, calcination temperature, the mass of adsorbent, and biogas flow rate on the H_2S removal.

3.5.1. Effect of Particle Size. Selection of particle size of an adsorbent is significant to enhance the adsorption ability of the material [30, 31]. Particles with larger diameter have lower adsorption ability of hydrogen sulfide from biogas than the particle of smaller size [32, 33]. According to our study, outcomes on hydrogen sulfide adsorption using red rock samples of different particle size are obtained as shown in Figure 5. It is seen that the sample of the smallest particle size of about $0.32\text{--}250\ \mu\text{m}$ calcined at 1000°C shows good

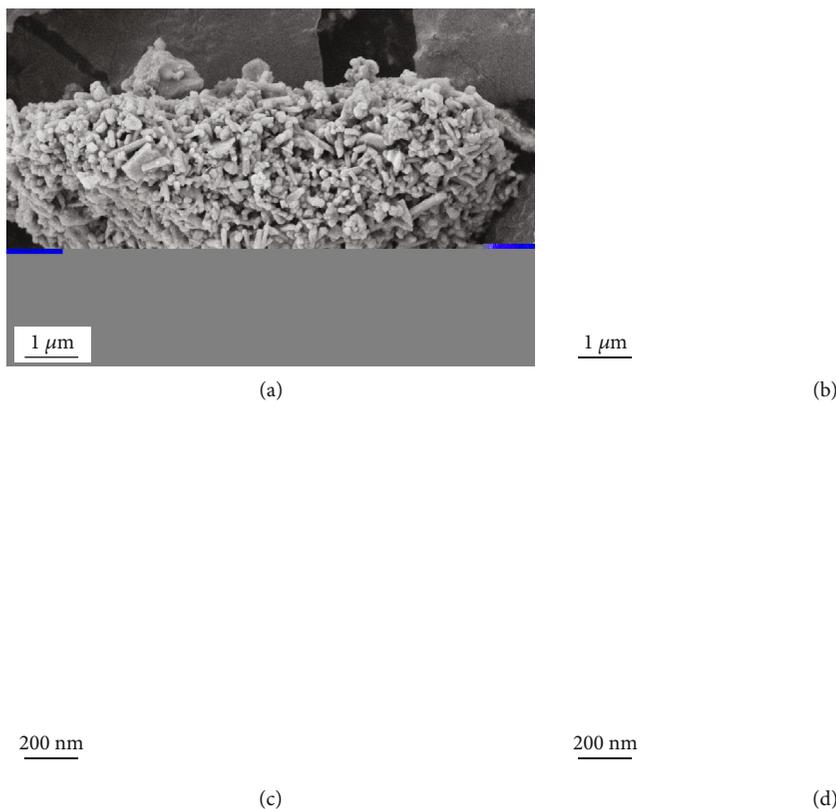


FIGURE 3: (a, b) Low-magnification (25.00 KX) and (c, d) high-magnification (50.00 KX) SEM images of RR-B and RR-C, respectively.

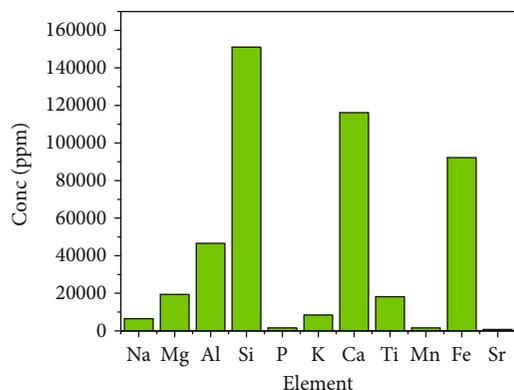


FIGURE 4: Elemental composition of red rock material calcined at a temperature of 1000°C.

adsorption ability; the latter is attributed to large surface area to volume ratio as per Table 2 compared to the rest.

3.5.2. Effect of Calcination Temperature. Among the five samples considered above, the best sample was 0.32–250 μm particle size. This sample was then tested for another parameter that was calcination temperature. The effect of the RR calcination temperature on the removal of H_2S from biogas was evaluated as the REs of a raw sample and samples calcined at 500, 750, and 1000°C were considered in Figure 6. The highest temperature provides higher removal efficiency of about 66.5%, and this is due to the reason that high temperature causes some unwanted material/compounds (volatile)

in the sample to evaporate and hence create more micropores for the hydrogen sulfide. The raw sample shows the removal efficiency of about 3.3% which is low compared to the calcined sample. This sample still contains some unwanted material like water; hence, they occupy the pores [34]. According to literature, higher temperature favors better sorption ability [35–37]. Therefore, sample 0.32–250 μm calcined under a temperature of 1000°C was tested for the next parameter.

3.5.3. Effect of Adsorbent Mass. Sample with particle size 0.32–250 μm calcined at 1000°C was tested for another parameter that is mass, as shown in Figure 7. When a higher amount of RR was used, then high adsorption capacity would be observed; this is in accordance to [38] while lowering the mass of RR on bed reactor decreases the amount of hydrogen sulfide adsorbed [31]. The removal efficiency of H_2S rises as the mass of adsorbent increases due to the increase in the interfacial external area for biogas to contact [31]. Therefore, hydrogen sulfide had more chance to contact with the adsorption site of RR material. From our study, the highest removal efficiency was obtained when 0.6 g of adsorbent was used. When the mass of adsorbent increased more than 0.6 g, there was no flowing of biogas due to the blocking of pores.

3.5.4. Effect of Biogas Flow Rate. Biogas flow rate influence on RR sorption ability was tested as showed in Figure 8, and particle size 0.32–250 μm calcined at 1000°C was used. It was observed that the ability of red rock material to adsorb H_2S

