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Research Article

Cryptogamic Packed Biofilter as Potential Adsorbent for CO_2, NH_3, and H_2S Impurities from Biogas

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

1. Introduction

The increase in energy demands due to population growth, depletion of worldwide oil reserves, and the problem of harmful emissions emanating from fossil fuel have put pressure on the world's countries to use renewable energy [1]. Biogas is one of the renewable energy sources. It provides the reliable option of a sustainable form of energy derived from energy crops, agricultural wastes, agroindustrial wastes, municipal waste, etcetera. The quality of biogas is an essential aspect for its energy and economic value; it depends on the percentage composition of methane, carbon dioxide, and hydrogen sulfide. Biogas produced from a digester is used mainly for cooking and rarely for heating, lighting, and electricity generation, simply because of the presence of hydrogen sulfide and other impurities which together lead to corrosion of metal components in engines and gas burners.

Typical raw biogas consists of about 55–65% methane, 30–45% carbon dioxide, traces of hydrogen sulfide, fractions of water vapors, and other contaminant gases [2]. The composition depends on the type of feedstock and anaerobic conditions. The H_2S and NH_3 components in biogas are (i) corrosive, which damages engines, and (ii) toxic [3]. In order to meet the standard for clean gas by increasing CH_4 concentration, the H_2S and other impurity content in biogas must be reduced. To achieve this, biogas must go through purification process [4]. Current technologies of biogas purification by removing H_2S, CO_2, and NH_3 employ the use of membrane separation, biological filters or activated carbon, and chemical liquids. These methods not only are costly but also have low removal efficiency [5]. Using iron oxide- (Fe_2O_3-) rich material is a simple, efficient method to remove H_2S in biogas since iron oxide readily reacts with H_2S to form iron sulfide (Fe_2S_3) when biogas passes through it [6].

$$Fe_2O_3 + 3H_2S = Fe_2S_3 + 3H_2O \tag{1}$$

$$2Fe_2S_3 + 3O_2 = 2Fe_2O_3 + 6S \tag{2}$$
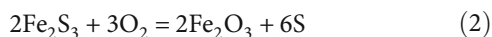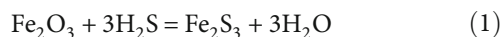
Soil can be considered the fine earth which covers land surfaces as a result of the in situ weathering of rock materials or the accumulation of mineral matter transported by water, wind, or ice. Soils rich in metallic oxides are found to be effective in the removal of H_2S [3]. A process of soil biofiltration involves absorption of gas dissolved in soil solution which occurs as discharge air (raw gas) passes through a series of moist, aerated biological material through perforated pipes arranged in a bed material [7]. Soil biofiltration is considered among the best available technology and more foolproof operation, because of lower investment and operating costs; they are most suitable where the pollutant loading is in low concentration or low volume discharge [8], whereby degradation rates typically range from 10 to $100\,gm^{-3}\,h^{-1}$ for common air pollutants. Primarily, they have been used for the control of foul odors and reduction in potentially toxic trace gases. The design employs either soil medium or compost in a system that makes use of natural soil processes for dissolution, adsorption, and microbial metabolism of inorganic gases and volatile organics present in the effluent air [7]. The desired filter volume depends mostly on the rate of the air pollutant loading (flow rate) relative to its degradation capacity and on the concentration of pollutants in raw gas. Another element that has been investigated for air biofiltration is biochar. It is known to be an efficient and cost-effective sorbent for different kinds of pollutant removal. Biochar contains unmodified activated carbon which in the presence of water slows down the degeneration process by promoting deposition of sulfur by mechanically removing sulfur from the active sites [9]. Sethupathi et al. [10] identified biochar as potential absorbers of CO_2 and H_2S from biogas. The study analyzed adsorption dynamics of biochar derived from four different types of oak materials.

Another practice of gas purification and air pollution control involves the use of active biological material. This process employs biomonitors, bioaccumulators, and bioindicators in filtering air impurities using naturally occurring plants (mosses, lichens, and liverworts) and inorganic materials. Lichens and mosses can be used as biomonitors of air pollution because they are highly dependent on atmospheric sources for nutrients and do not shed plant parts as readily as vascular plants [11]. These organisms are scientifically referred to as cryptogams. They are made up of photoautotrophic communities, consisting of cyanobacteria, algae, fungi, lichens, and bryophytes, that is, liverworts and mosses in variable proportions [12]. These communities can provide food webs by photosynthesis and nitrogen fixation, which is particularly essential in arid regions and other terrestrial environments with a low abundance of organic nutrients. Cryptogams are estimated to be responsible for almost half of the total terrestrial biological nitrogen fixation of $\sim 49 \cdot 10^9\,kg\,year^{-1}$ and carbon uptake of $\sim 3.9 \cdot 10^9\,ton\,year^{-1}$ which amounts to $\sim 7\%$ of the net primary production of terrestrial vegetation [13].

These organisms are also well known to accumulate and retain a variety of contaminants, which make them useful in recording relative spatial and temporal deposition patterns of these contaminants. Integrating plants and soil biofiltration for the elimination of technogenic and volatile organic gases (VOC) has been studied to provide means of biofiltration without the use of consumables [14, 15]. Incorporating different media in a packed bed filter has shown successful results in biofiltration for a wide range of air pollutants and VOCs [7, 16]. Natural organic medium primarily composed of peat, compost, leaves, wood bark, and soil has been studied for the removal of toluene-contaminated air and VOCs [17]. In this study, we use the already analyzed soil physical-chemical properties in order to determine the effective optimal composition for improved removal efficiency of the biofilter. The effects of soil type, soil mass variation, and analysis of each substrate for the removal of CO_2, H_2S, and NH_3 in the biofilter were illustrated. Also, the effect of gas flow rate using the soil with high removal efficiency was evaluated. The design and fabrication of the filter were established by considering the high surface area for reaction, pressure drop, moisture retention capability, and production rate of the biodigester.

2. Material and Methods

2.1. Soil Collection. The soil samples and profile statistics were collected from Tanzania Agricultural Research Institute located in Tanga, Tanzania, as part of the soil survey profile for Kwaraguru Sisal Estate, Tanga. In total, four soil samples were identified as likely candidates for evaluation based on guidelines of soil classification using World Reference Base for Soil Resources 2014 Edition [18]. The selected soil sample contained a high amount of metallic micronutrients per kilogram (the amount of metallic nutrient a plant can absorb via its roots), percentage of soil organic carbon, and carbon to nitrogen ratio. The soil samples with the high composition of extractable micronutrients (Fe, Zn, Cu, and Mn) from each profile were selected for this study. Other properties, including the percentage of organic carbon (%C), carbon to nitrogen ratio (C/N), and pH, were also considered for the selection. The selected soils were named T1, T2, T3, and T4 as depicted in Table 1.

2.2. Filter Preparation. To construct a prototype of the filter, each substrate, i.e., soils T1, T2, T3, or T4; biochar; and moss, was pretreated after collection, in order to remove unwanted components like roots, plastics, and leaves. The filter was designed to provide a high specific surface area for gas reaction with a low-pressure drop over the packed column. A combination of high content of active ingredients favors a substantial sulfide-binding capacity [19]. Each filter contained one of the four types of soil (T1, T2, T3, or T4) sieved at less than $400\,\mu m$ with variable mass (100 g, 150 g, or 200 g); 100 g of biochar (charcoal) dust sieved at less $350\,\mu m$; and 545 g of naturally grown moss plant collected from damp sidewalk during the rainy season. The packed bed arrangement of the substrates was adopted from Pham et al. [20]; the study demonstrated removal of H_2S using

TABLE 1: Soil database and profile information.

| Coordinates (Lat-Long)	-5.42057° S, 38.52185° E	-5.42519° S, 38.52794° E	-5.48036° S, 38.52422° E	
Appearance	Dark reddish-brown	Very dark greyish brown	Dark reddish-brown	
Sample name	T1	T2	T3	T4
Depth (cm)	0-15/20	20/25-40	0-15/20	15/20-40
Clay (%)	62	40	50	58
Texture class	Clay	Clay	Clay	Clay
Bulk density (g/cm^3)	1.02	1.34	1.18	1.21
pH H$_2$O	5.2	6.9	5.4	5.4
Exch. Cu (mg/kg)	7.47	7.77	2.25	1.5
Exch. Zn (mg/kg)	0.99	0.48	1.62	0.36
Exch. Mn (mg/kg)	16.5	47.1	117.0	39.3
Exch. Fe (mg/kg)	33.99	31.29	51.39	57.69
Organic C (%)	1.49	1.36	1.77	1.10
C/N	6.77	4.69	8.05	6.47
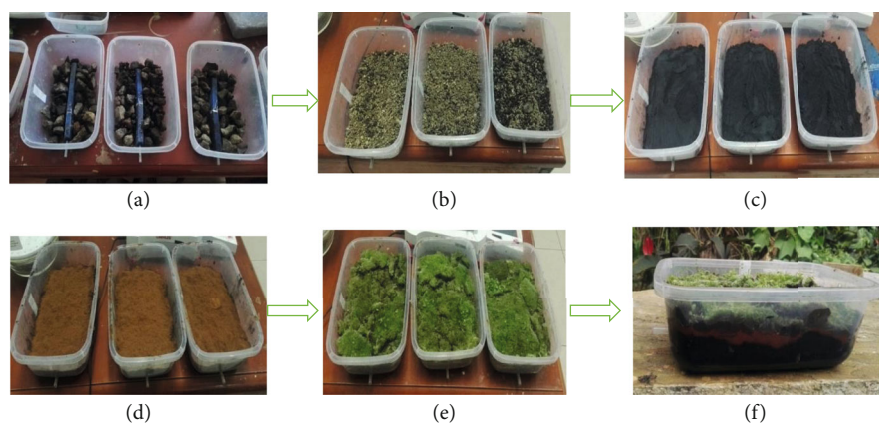
FIGURE 1: Preparation of the biofilter: (a) inlet through aeration; (b) gravel packs (200 g); (c) biochar dust (250 nm/100 g); (d) soil substrate (100 g); (e) moss substrate (545 g); (f) filter open.

local soil materials from biogas produced by anaerobic digestion of animal wastes. In this study, 700 g layer of small and medium gravels was added above the aerator to prevent blockage by overlying filter material. Moss plant was added as a top layer, with soil and biochar dust as preceding layers below it in order to ensure active gas exchange, growth, and sustainability of the filter. The substrates were packed into polyplastic containers each with the dimensions (25 cm × 16 cm × 9 cm) with an airtight cap to cover the top part; the container was transparent to allow just enough light in the filter to aid photosynthesis reaction of moss plants. An inlet port for the introduction of unpurified gas was inserted at the bottom part connected to the aerator (20 cm long) to ensure homogeneous distribution of the inlet gas across the face of the bed. A step-by-step preparation of the filter is as shown in Figure 1.

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

ensure all the humid condition present in the moss plant is preserved. The humid condition in the filter is essential to ensure microbial action and enhance the sorption of CO_2 and H_2S. Xie et al. [21] showed that the presence of soil moisture content results in increased removal capacity for H_2S in a soil biofilter. The presence of water has also shown a beneficial effect on overall temperature catalytic performance of activated carbon for the oxidation of H_2S to sulfur [9]. After fabrication, the filter was then closed and sealed to begin measurements. It was designed to require no energy during its operation.

2.3. System Operation. Two biogas reactors L1 and L2 available at private premises were used for experimental testing of the biofilter. Table 2 depicts features of both digesters as well as the average composition of raw biogas which was comparable by methane and carbon dioxide contents but slightly different by ammonia and hydrogen sulfide concentrations. In our on-site tests, biogas flow was allowed to pass through the filter media contained in a rectangular plastic container. The block diagram of the experimental setup is shown in Figure 2.

TABLE 2: Domestic biodigesters used for the analysis.

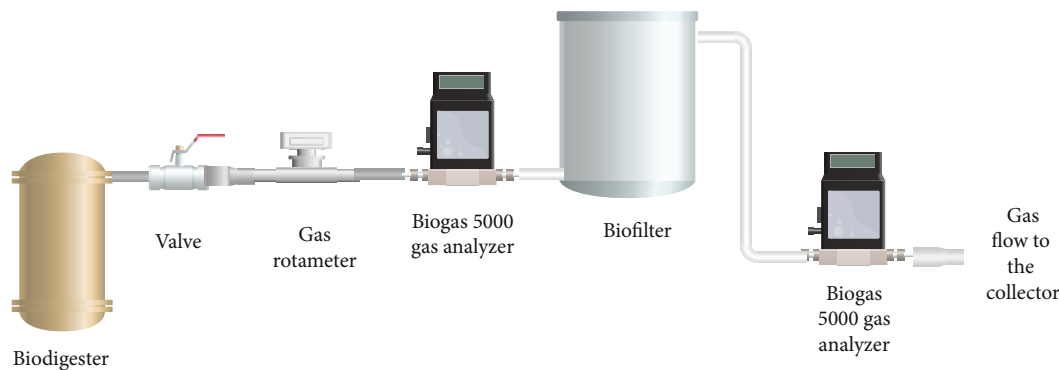| Digester type	Digester volume (m^3)	Feedstock	Volume gas column (m^3)	Max pressure (mbar)	Raw gas composition
L1	16	Domestic sewage and garden wastes	4	107.8	68–72% CH_4, 38–40% CO_2, 6–14 ppm NH_3, 498–913 ppm H_2S
L2	9	Rougher garden wastes and overflow from L1	0.8	84.3	64–66% CH_4, 34–38% CO_2,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

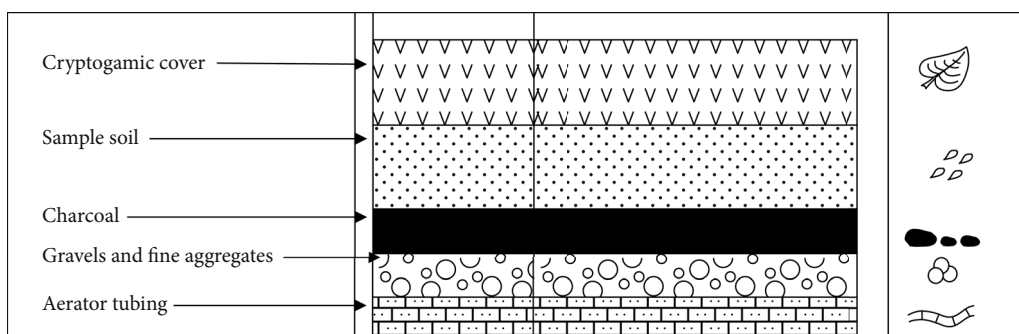FIGURE 2: Photo and schematic diagram of the experimental setup.

FIGURE 3: Schematic diagram of substrate arrangement in the filter.

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

The tests were divided into three parts. The first part was conducted to analyze the effect of soil type on biogas purification in order to determine the sorption capacity of the adsorbents. The second part was aimed at analyzing raw gas adsorption by each substrate, and the third part was at summarizing the role of each adsorbent in gas purification which was conducted with flow rates of 80 and 100 ml/min during times 0-150 min for each filter in ambient condition. The arrangement of these substrates in the filter is as shown in Figure 3.

In order to examine the performance of each substrate in a filter, raw biogas was allowed to pass through a 5 g sample packed in airtight 5 ml plastic tube at a constant flow of 100 ml/min; the inlet and outlet concentrations of H_2S, CO_2, and NH_3 were measured; and the readings were recorded in a 10 min interval for 80 min. A small sample mass had to be used in order to ensure the maximum surface area for adsorption and to avoid a very high-pressure drop which is not recommended for biofilter operation. For example, Wellinger and Lindberg [22] and Abatzoglou and Boivin [3] showed from various studies that commercially packed biofilters are engineered to provide high specific surface area, having a low-pressure drop, and together with a high content of active ingredient provide high sulfide-binding capacity.

2.4. Filter Performance Parameters. The performance of the developed biofilter was determined in terms of removal efficiency (RE) and sorption capacity (SC). The CO_2, NH_3, and H_2S concentrations of treated gas at the outlet were analyzed at 10 min intervals for each test; RE and SC were calculated using Equations (3) and (4), respectively, whereby C_i and C_f are the initial and final concentration of H_2S (CO_2 or NH_3) as measured before and after filtration, respectively;
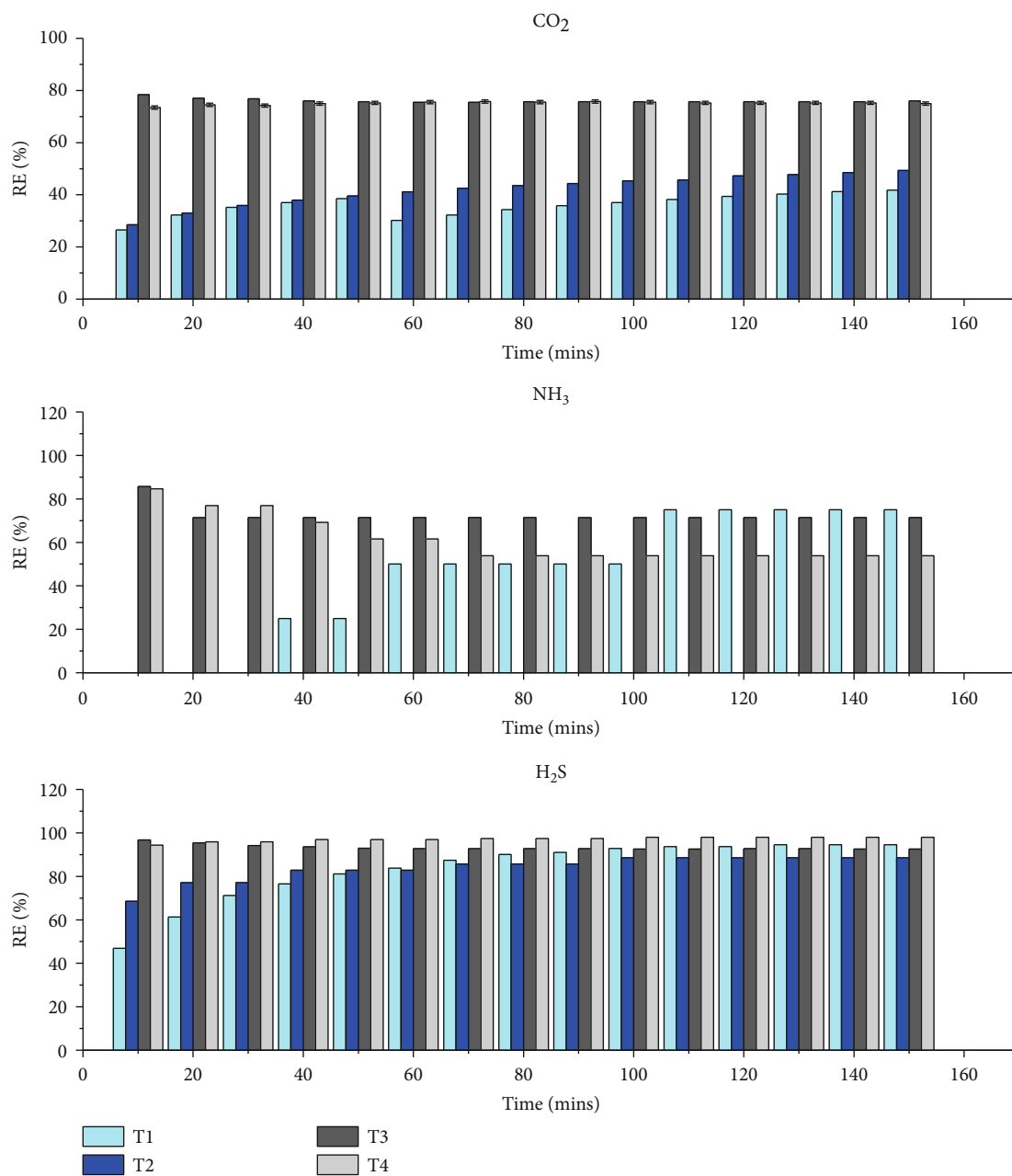
FIGURE 4: Biogas purification by filters with different soil samples: RE versus operating time. Test conditions: $Q = 80$ ml/min, $m = 100$ g, $T = 19°C$, $C_0 = 36.4\%$ for CO_2, 13 ppm for NH_3, and 836 ppm for H_2S.

TABLE 3: Soil-type performance in biogas purification (RE) average over an operating time of 2.5 hrs ($Q = 80$ ml/min).

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

[*]nd: not determined.

Q is the flow rate (m^3 h^{-1}), M is the atomic mass of sulfur, Vmol is the molar volume of the gas (l mol^{-1}) under standard conditions. A breakthrough time (BT) in hours was recorded as the time when C_f approached 50% of C_i, where no significant adsorption of sulfur by the substrate was observed.

$$RE\,(\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad (3)$$

$$SC\left(\frac{g\,sulfur}{100g\,sorbent}\right) = Q \times \frac{M}{Vmol}\,(C_i - C_f)BT \qquad (4)$$
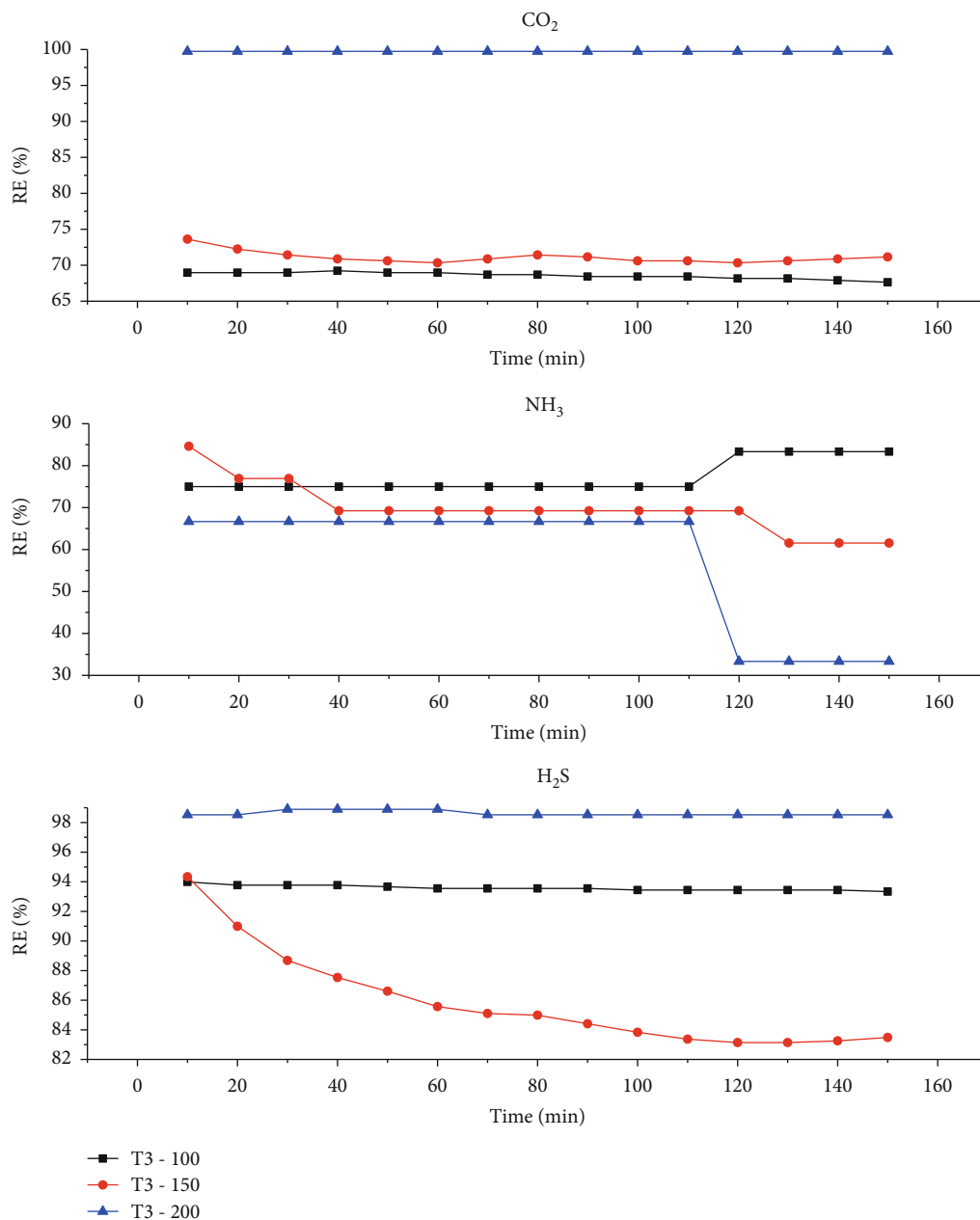
FIGURE 5: Soil mass effect of the filter RE. Test conditions: $Q = 100$ ml/min, $m_1 = 100$ g, $m_2 = 150$ g, $m_3 = 200$ g, $P = 10$ kPa, $C_0 = 37.5\%$ for CO_2, 13 ppm for NH_3, and 836 ppm for H_2S.

3. Results and Discussion

3.1. Effect of Soil Type on Biogas Purification. This experiment was conducted to assess the performance of the filter in terms of removal efficiency for CO_2, H_2S, and NH_3 impurities present in the biogas. Figure 4 shows the removal efficiency for CO_2, H_2S, and NH_3 from each soil type at a constant flow rate, with the test conditions and results summarized in Table 3. The results indicate that filters with T3 and T4 soils had the most substantial average removal of CO_2 at 76% and 75%, respectively. T3 filter also showed a significant RE of NH_3 at 72% on average over the entire period than other soil types. For H_2S removal, filters T4 and T3 showed the largest RE at 97% and 93%, respectively. The reason for higher RE exhibited by soils T4 and T3 is presumably due to the highest total content of extractable iron compared to T1 and T2, as shown in Table 1. As has been discussed, according to reaction Equation (1), high iron contents in the soil contribute to more significant interaction with H_2S impurities. Presence of other extractable micronutrients (Zn, Cu, and Mn) also favors reaction with H_2S.
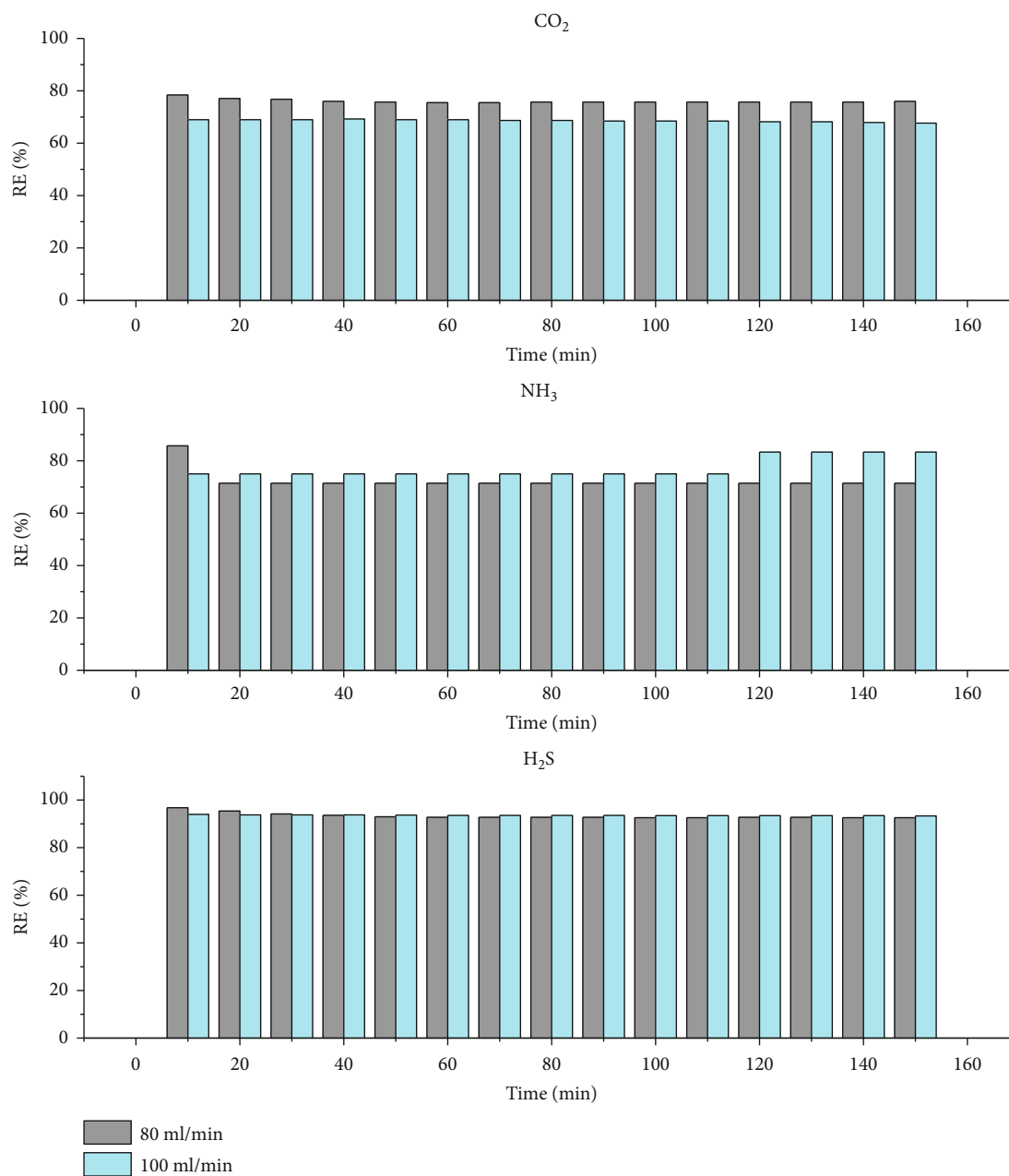
In order to elucidate the role of each substrate, special tests were conducted as described in Section 2.3; the SC of each biofilter component was calculated by using Equation (4).

FIGURE 6: RE of the filter T3-100 at two different flow rates (80 and 100 ml/min). Test conditions: Q_1 = 80 ml/min, Q_2 = 100 ml/min m =100 g, P = 10 kPa, C_0 = 37.7% for CO_2, 12 ppm for NH_3, and 915 ppm for H_2S.

The test results accord well with an investigation by Rodriguez et al. [23] where it was shown that H_2S and S_2 reacted faster with CuO and ZnO than corresponding sites of alumina (Al_2O_3) based on the bandgap size and chemical reactivity. Also, it was further observed by Ko [24, 25] that iron-rich and zinc-containing soils effectively removed H_2S from coal-derived natural gas. The soil T3 showed higher interaction with H_2S. The dark reddish-brown coloration of the soil indicates richness in the crystalline structure of iron oxide minerals which have a strong influence on H_2S removal capacity [19]. Also, Lasocki et al. [26], observed that the iron oxide present in soils and activated carbon (charcoal) as beds

in filters reduced almost 100% of H_2S in a 30 min exposure period in the laboratory-scale investigation.

Other factors that contributed to better performance of T3 soil were high levels of soil organic matter, organic carbon percentage, and C/N ratio of the soil compared to other soils. Presence of organic matter improves soil aggregate and structural stability which are significant for infiltration of water and aeration into the soil, thus enabling the high surface area of reaction [27]. Soil organic carbon is vital in improving soil structure and provides habitat for soil biota, which together ensures sustainable yields as they retain water and nutrients [28, 29]. The level of C/N in the soil determines the rate of

TABLE 4: Effect of soil mass and biogas flow rate on the biofilter T3 performance; H_2S removal efficiencies are given as average values over 2-hour operating time.

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

decomposition of organic matter and soil productivity, which was studied by using paddy fields by Li et al. [30]. Therefore, T3 soil was subjected to further tests in the effect of soil mass and flow rate to the removal efficiency.

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

During operation time of 150 min, the outlet impurities were recorded as the raw gas passed into the filter. Figure 5 shows the removal efficiency of CO_2, NH_3, and H_2S gases. For CO_2, the removal efficiency was approximately 99.7% for T3-200 over the operation time. When the mass of the soil was further lowered to 150 g, the removal efficiency dropped to about 75% and further to nearly 70% for the filter with 100 g soil.

For the case of NH_3, RE was 83% but dropped to 33% for T3-200 and as high as 83% to 77% drop for T3-150. The filter T3-100 had a maximum RE of 80% before saturation. After 120 min, no more NH_3 adsorption was observed. We suppose this sharp decrease could be due to the drop in the initial concentration of the gas to the lowest amount recorded of 7 ppm and that low ammonia concentration measurement occurred at the sensitivity limit of the gas analyzer. T3-100 has a large surface area of reaction, unlike other filters with substantial mass, which are highly compacted thus having less adsorption rate. As it was demonstrated by Kent et al. [31], filter beds with small particle size not only offer a high specific surface area for reaction and thus favoring nitrification and microbial activity but also tend to constitute a greater resistance to gas flow which increases as biomass grows in bed porosities [32]. On the other hand, large particles have low-pressure drop since the gas flow is not blocked but offer fewer surface sites for oxidation reaction; therefore, it can lead to lower elimination performances [33]. Also, NH_3 has a low Henry's constant ($H_{20°C} = 5.6 \times 10^{-4}$) [34] and a protonation constant $pK_{a, 20°C}$ of 9.23 [35]. These

values make NH_3 in biofilters to be partly retained onto the surface of carrier material by adsorption and by absorption of water fraction of the material [36].

The T3-100 filter showed higher RE in H_2S than T3-150 and T3-200, which can be explained by the availability of high surface area of adsorption between the gas molecules and the soil adsorbent containing a high content of iron and other cations, e.g., Cu and Zn. T3-200 due to a large mass of soil content has the highest gas retention time of all the filters, as it takes longer for the gas reaction to complete. The large mass of soil may also lead to clogging. It can be effective if the soil is evenly dispersed to allow more gas retention time. The higher retention time was effective in H_2S elimination capacity as it was studied by Yang and Allen [32].

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

3.3. Effect of Biogas Flow Rate on the Biofilter T3 Removal Efficiency. The H_2S, CO_2, and NH_3 removal were further analyzed for filter T3 by considering variation in flow rates of 80 ml/min and 100 ml/min. The filter performance with the soil mass 100 g (T3-100) is shown in Figure 6. As is seen, quite steady RE behavior is upheld for all three impurities, except a small and casual variation for NH_3 that can be attributed to a small but changeable amount (7–13 ppm) in the raw gas. The CO_2 removal is affected by the flow rate, the RE lowered by 7% from 80 to 100 ml/min. In the case of H_2S, the change of flow rate practically does not influence the RE that remains constant ≈94% during the filter operating time. A summary of removal efficiency at both flow rates is given in Table 4. Also, the effect of the soil mass is taken into account.

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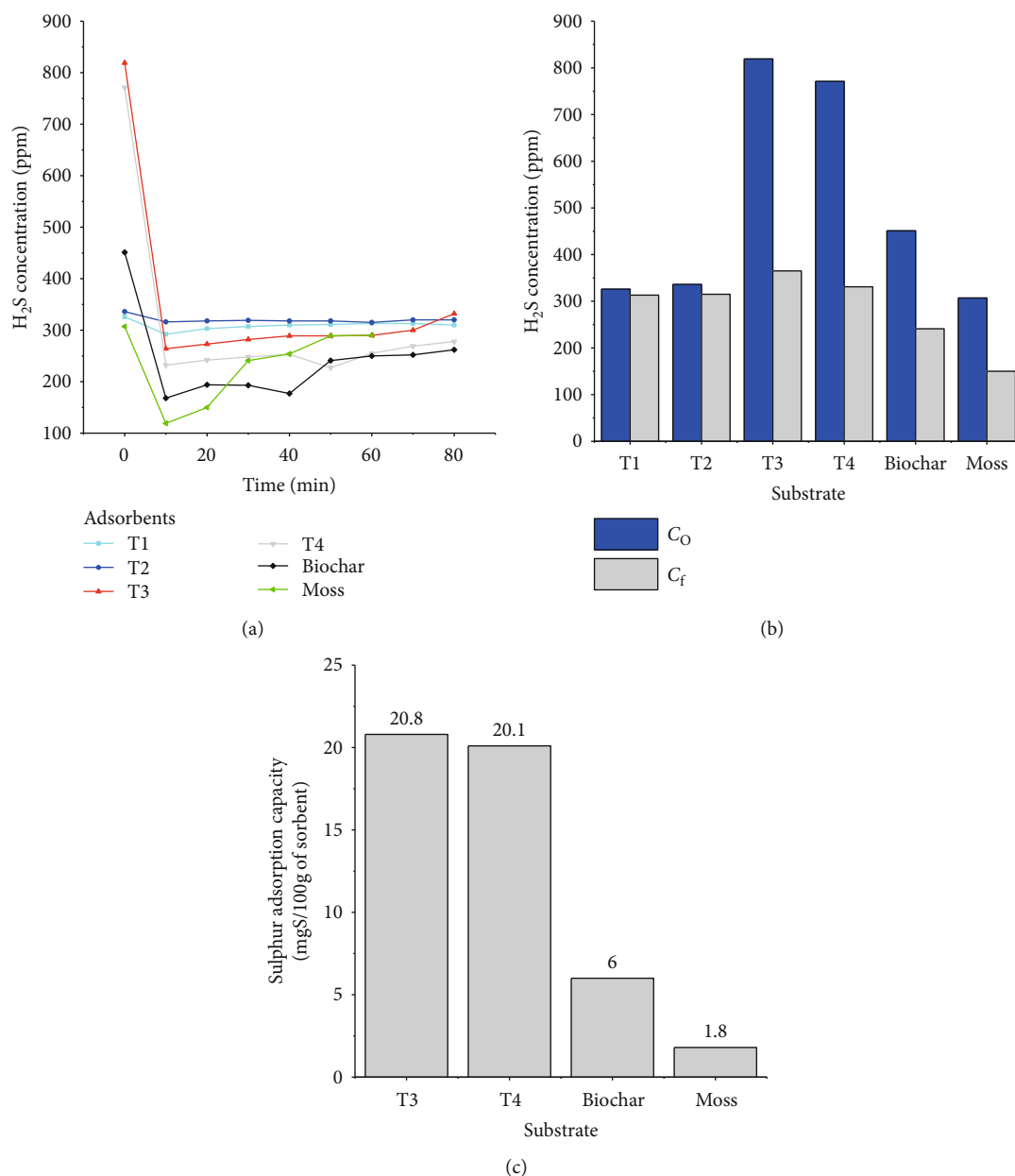
(a)

(b)

(c)

FIGURE 7: Sulfur removal by various adsorbents: (a) breakthrough curves, (b) H_2S absorption over breakthrough time, and (c) sorption capacities. Test conditions: $Q = 100$ ml/min, $m = 5$ g, $C_0 = 307$-819 ppm for H_2S, and time $= 80$ min.

T3-100. Meanwhile, with a low flow rate for T3-100 and T3-150 filters, high RE is observed. This can also be as a result of having sufficient reaction time for the adsorption of CO_2 by the substrate.

On average, the RE for NH_3 is high with T3-100 at 100 ml/min and drops as the mass of the filter increases (T3 − 150 > T3 − 200). Moreover, with the flow of 80 ml/min, there is a slight difference in RE for T3-100 and T3-150, but it drops for T3-200. Shoda [37] and Joshi et al. [38] demonstrated on a field-scale peat biofilter that NH_3 removal along with sulfur compounds can also be attributed to the adsorption by the acidic nature produced during oxidation of sulfur compounds.

By increasing the flow rate, the gas reaction time increases for the filter with larger mass (T3-150 and T3-200) and lower

risk of clogging. But for the filter with small mass, the effect is reversed as more gas will pass through without being adsorbed by the soil adsorbent. For the T3-100 filter, the RE was considerably high for a low flow rate than a high flow rate. This allows a large number of particles present to interact with H_2S gas, offering more time for oxidation to occur. With a low flow rate, maximum gas reaction time was observed. These results are in agreement with studies from Chung et al. [39] and Singh and Mandal [40], whereby data on H_2S removal by combined chemical and microbial solution showed that RE for H_2S increased with increasing gas reaction time. In the investigation on operational parameters of biofiltration design by Yang and Allen [32], it was observed that an increase in loading rate results in a decrease in gas retention time, due to insufficient reaction time between H_2S molecules
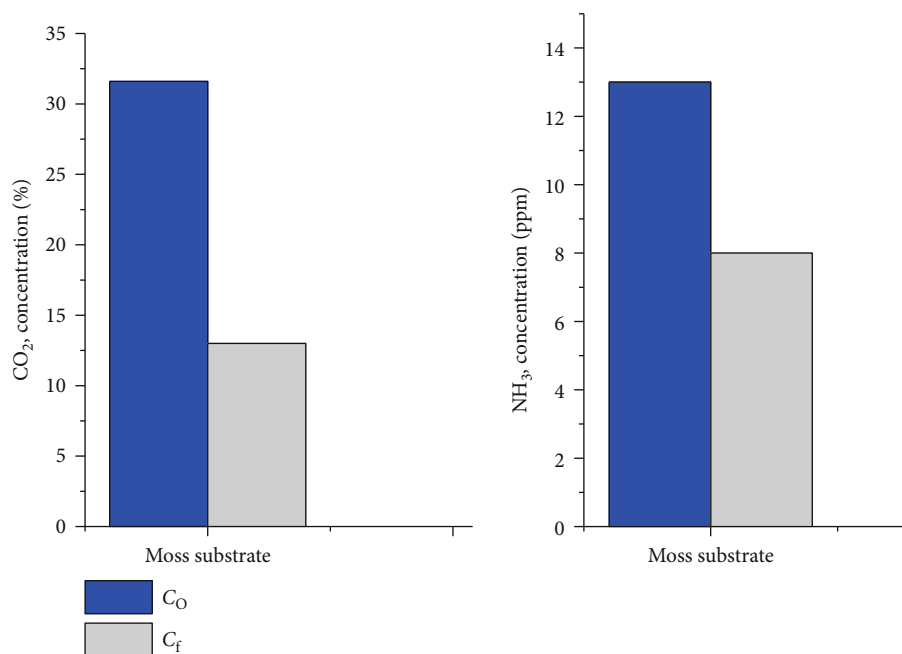
FIGURE 8: Adsorption of CO_2 and NH_3 by moss substrate. Test conditions: $Q = 100$ ml/min, $m = 5$ g, $C_0 = 307$-819 ppm for H_2S, and time = 60 min.

and the biomass in the filter. Thus, H_2S RE can be improved by either reducing the flow rate or increasing the soil volume. As seen in Table 4, the best performing filter for all gases by considering average RE was T3-100. Other filters showed better RE for one type of pollutant but less for the other type measured at either of the flow rates. For example, T3-200 showed high RE for CO_2 and H_2S but less with NH_3.

3.4. Analysis of the Function of Each Substrate

3.4.1. Sulfur Adsorption Performance of Various Adsorbents. The breakthrough time is used to specify the saturation time of the substrate before it needs regeneration or replacement. Longer breakthrough time implies a better adsorption capacity of the particular substrate (adsorbent) [41]. It also implies a shorter reaction time. Variations of the adsorbate concentration against the operating time of a filter are known as breakthrough curves [10]. These curves are presented in Figure 7(a) for different biofilter substrates, the soil T3, biochar, and moss. The sample was considered saturated when the outlet concentration reached 50% of the inlet.

The H_2S breakthrough time for adsorbents T3 and T4 was both about 80 min, after which a minimal variation in sulfur adsorption was observed. Also, for the case of biochar and moss, the H_2S breakthrough time (BT) was 50 min and 20 min, respectively. For other adsorbents, T1 and T2, a small change in their concentrations was observed; thus, no significant adsorption was detected. The adsorption breakthrough time of T3 and T4 was higher than that of other adsorbents (substrates). A comparison between initial and final H_2S concentrations is shown for the substrates in Figure 7(b). The sulfur sorption capacity of each substrate was calculated using Equation (4) and indicated as the amount of sulfur adsorbed per 100 g of the sorbent in Figure 7(c). As seen,

the soils T3 and T4 retain the highest H_2S amount, 20.8 and 20.1 g S/100 g, respectively, compared to other adsorbents whereas T1 and T2 soils are practically unable to adsorb sulfur. Regarding biochar and moss substrates, H_2S was partly retained with a sorption capacity of up to 6.0 and 1.8 g S/100 g, respectively. The results are comparable with data by Sahu et al. [42], whereby the sorption capacity of red mud (RM) sample used for H_2S removal was 2.1 g-H_2S/100 g of RM. High sorption capacity by T3 and T4 is comprehensible, as they both have a high total content of extractable cation, specifically iron, and high C/N compared to other soil substrates as shown in Table 1.

Summarizing contributions from the three substrates; (soil T3, biochar, and moss), the designed SC biofilters T3-100 and T4-100 can be estimated to remove a total of 10.8 and 10.7 g S, respectively.

3.4.2. Moss Substrate Performance in CO_2 and NH_3 Removal. The capacity of a moss substrate on removing CO_2 and NH_3 from biogas was tested under the same conditions as described in the previous subsection about H_2S sorption. A 59% drop in CO_2 concentration and 38% for NH_3 were recorded during the 60 min of the experiment Figure 8. For the case of CO_2, moss plants like most cryptogams account for the largest net carbon uptake (photosynthesis minus respiration) from the atmosphere [43, 44]. The present study demonstrated moss to be very effective in CO_2 adsorption from raw biogas for 60 min. A low adsorption rate for NH_3 is mainly because moss is a nonvascular plant as most ammonia needs to be converted first to ammonium and nitrate by nitrifying bacteria, and absorption by the plant from the soil is done by roots [38].

Ammonium is usually toxic to plants in any appreciable quantity as it causes degeneration and morphological

TABLE 5: Absorption properties of the cryptogamic filter compared to other biofilters.

Bed type/ adsorbent	Gas	Impurity gas	Loading rate	RE (%)	Elimination capacity	Disadvantage	Reference
Peat biofilter	NH_3	20 ppmv	$1.8\,g\,m^{-3}\,hr^{-1}$	80	$41\,g\,m^{-3}\,d^{-1}$	Overloads at a loading rate of $7.9\,g\,m^{-3}\,hr^{-1}$. Prone to channeling and maldistribution. Limited ability to neutralize acidic degradation products	[49]
Perlite biofilter	NH_3	20-50 ppmv	$8.6\,g\,m^{-3}\,d^{-1}$ and $21.5\,g\,m^{-3}\,d^{-1}$	99.5	NA	Production of NO and NO_2 at the outlet	[38]
Cow manure compost	H_2S	~ 1500 ppm	$58\,m^3\,h^{-1}$	80	$16–118\,g\,m^{-3}\,h^{-1}$	High operating costs, clogging to deposition of elemental sulfur	[50]
Red mud	H_2S	200 ppm	0.0048	NA	$2.1\,g\,H_2S/100\,g$	Due to the small mass of adsorbent, H_2S removal was low	[42]
Biomass ash	CO_2 and H_2S	100–600 ppm H_2S, 33–35% CO_2	0.56-$1.25\,kg\,H_2S\,t^{-1}$ ash, $35\,kg\,CO_2\,t^{-1}$ ash, and $135\,kg\,CO_2\,t^{-1}$ ash	50 for H_2S, not feasible for CO_2	NA	Not feasible for CO_2 removal, ashes could not be reused for as fertilizer	[51]
T3, T4 soil substrates	H_2S	771-819 ppm	$0.0048\,m^3\,h^{-1}$	93, 97	20.8, 20.1 g S/100 g	A constant flow rate $<0.006\,m^3/hr$ to prevent large pressure drop	This study
Moss substrate	CO_2, NH_3, H_2S	CO_2 31.6%, H_2S 307 ppm, NH_3 13 ppm	$0.006\,m^3\,h^{-1}$	59 CO_2, 38 NH_3, 68 H_2S	6.0 g S/100 g of sorbent	The flow rate $<0.0048\,m^3/hr$ to prevent intoxication of microbes by NH_3 and H_2S present	This study
Cryptogamic filter	CO_2, NH_3, H_2S	CO_2 38%, NH_3 8.7 ppm, H_2S 819 ppm	$0.006\,m^3\,h^{-1}$	99.7 CO_2, 77.2 NH_3, 98.6 H_2S	11 g S/100 g	It does not work on high pressure, high flow rate operation, and requires water scrubber for removal of excess oxygen	This study

*NA: not applicable/addressed.

abnormalities [45, 46]. However, studies from Burkholder [47] showed that cultured moss had a high tolerance to ammonium ion (NH_4^+). It also enhanced the growth of some species of moss, e.g., fast-growing aquarium moss [48]. The NH_3 absorption can also be attributed to the thin layer of soil by which the moss is partially rooted.

3.5. Comparison of Biogas Purification with Other Biofilters of Different Media. Biological techniques can be the best alternative in the reduction of impurities in biogas, because the use of chemicals is limited, and it is considered economical and environmentally friendly. Investigations of different media for biogas purification in comparison to our study are summarized in Table 5.

In this study, NH_3 was removed to up to 77.2% at a constant flow of $0.006\,m^3\,h^{-1}$ (100 ml/min). For CO_2 and H_2S removal, the physical and chemical properties of biochar in the filter have significantly improved the adsorption capacity.

Sethupathi et al. [10] observed that the adsorption performance of a fixed bed column was significantly improved by physical and chemical properties of biochar on CO_2 and H_2S removal. It also revealed that biochar has a relatively low effect on CH_4 adsorption. Therefore, CH_4 content is unaffected during the whole adsorption process. Fernández-Delgado Juárez et al. [51] in their study on biogas purification with biomass ash found that the ash was successful in removing both CO_2 and H_2S, but to an extent, CO_2 removal was affected by high filter rates. Our study has addressed the flow rate to ensure maximum gas reaction time to allow considerable adsorption of CO_2 by biochar and moss substrates. The presence of moisture by which cryptogams thrive provides a humid condition for further removal of CO_2 and H_2S gases. The filter has integrated the physical and chemical properties of these substrates to facilitate the removal of these impurities from the gas. Other multiple gas removal filters were designed for the removal of more than one pollutant from the gas; results have shown significant removal for one gas but relatively poor for the other gases [51]. The primary advantages of biological filters were low energy requirements, mild operations, and regeneration capability of the materials [52, 53]. The disadvantage of using these methods was the low flow rate required for operation, additional nutrients were required, clogging of the bed due to sulfur deposit, and a small amount of O_2, N_2, and moisture were left in the treated biogas [6].

4. Conclusion

Biofiltration system integrated with four types of soils, T1, T2, T3, or T4, with biochar and cryptogamic cover, was designed and tested on-site for removal of biogas impurities in the form of CO_2, H_2S, and NH_3. The function of each substrate was elaborated via a special experimental arrangement. Among the samples, the T3 and T4 soils demonstrated the best H_2S removal with sorption capacities of 20.8 and 20.1 g S/100 g and RE of 93% and 97%, respectively. This good performance of the soils attributed to their high iron content, large cation exchange concentration, and organic

carbon percentage. Moss and carbon-based material (biochar) showed inadequate H_2S removal, indicating that pure physical adsorption was not efficient on digesters operating at low pressures such as in typical farm. Moss substrate had significantly high CO_2 RE of 59% and as low as 38% for NH_3 during the 60 min of the experiment.

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

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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