Research Article

Enhancement of Methane Concentration by Removing Contaminants from Biogas Mixtures Using Combined Method of Absorption and Adsorption

Muhammad Rashed Al Mamun and Shuichi Torii

Department of Mechanical System Engineering, Graduate School of Science and Technology, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan

Correspondence should be addressed to Muhammad Rashed Al Mamun; rashedshahi@gmail.com

We report a laboratory scale combined absorption and adsorption chemical process to remove contaminants from anaerobically produced biogas using cafeteria (food), vegetable, fruit, and cattle manure wastes. Iron oxide (Fe_2O_3), zero valent iron (Fe^o), and iron chloride ($FeCl_2$) react with hydrogen sulfide (H_2S) to deposit colloidal sulfur. Silica gel, sodium sulfate (Na_2SO_4), and calcium oxide (CaO) reduce the water vapour (H_2O) and carbon dioxide (CO_2). It is possible to upgrade methane (CH_4) above 95% in biogas using chemical or physical absorption or adsorption process. The removal efficiency of CO_2, H_2S, and H_2O depends on the mass of removing agent and system pH. The results showed that $Ca(OH)_2$ solutions are capable of reducing CO_2 below 6%. The H_2S concentration was reduced to 89%, 90%, 86%, 85%, and 96% for treating with 10 g of $FeCl_2$, Fe^o (with pH), Fe_2O_3, Fe^o, and activated carbon, respectively. The H_2O concentration was reduced to 0.2%, 0.7%, 0.2%, 0.2%, and 0.3% for treating raw biogas with 10 g of silica gel and Na_2SO_4 for runs R1, R2, R3, R4, and R5, respectively. Thus, given the successful contaminant elimination, the combined absorption and adsorption process is a feasible system for biogas purification.

1. Introduction

The current use of fossil fuels is rapidly depleting the natural reserves and would be available to mankind only for a limited time due to their diversified use in every country [1]. Because of the natural formation of coal and oil however it is a very slow process which takes millions of ages to become so. Recently, sustainable solid waste management is becoming an issue of global concern due to the steady increase in population, urbanization, and industrialization. Therefore, the increasing concentration on the emission of greenhouse gases like carbon dioxide and methane having strengthened the interest for research effort is put into finding renewable fuels nowadays to replace fossil fuels [2, 3]. Renewable fuels are in balance with the environment and contribute to a far lesser extent to the greenhouse effect. Biogas is such a renewable fuel, an energy source that can be applied to its versatility of use in gas engines, microturbines, electricity generation,

and fuel cells for continuous energy production [4–8]. It is a combustible gas mixture produced by the anaerobic fermentation of biomass by bacteria and takes only a relatively short time to form. The biogas mainly consists of 60–70% combustible methane (CH_4) and 40–30% noncombustible carbon dioxide (CO_2) along with smaller amounts of other gases such as oxygen (0-1%), nitrogen (<1%), siloxanes (0–0.02%), halogenated hydrocarbons (VOC, <0.6%), carbon monoxide (CO, <0.6%), hydrogen sulfide (H_2S, 0.005%–2%), and water vapours (H_2O, 5–10%) [9–13]. CH_4 combusts very cleanly without any soot particles or other pollutants, making it a clean fuel. On average, the calorific value of biogas is 21.5 MJ/m^3 whereas that of natural gas is 35.8 MJ/m^3 [14]. The incombustible part of biogas, CO_2, lowers its calorific value. By removing CO_2 from the biogas the calorific value is increased. Besides CO_2, biogas contains small amounts of hydrogen sulfide (H_2S). When water is present, H_2S forms sulfuric acid (H_2SO_4), which is highly corrosive,

rendering the biogas unusable. Currently, biogas which has been stripped of H_2S is mainly used in gas turbines to produce electricity. However, most energy is lost as heat in this process which results in a low overall efficiency. Stripping CO_2 and H_2S from biogas is the so-called methane enhancing of biogas. By upgrading biogas to natural gas quality, containing more than 90% CH_4 [15], it is suitable for more advanced applications in which the heat is not wasted, resulting in a higher efficiency.

The process of enhancing biogas generates new possibilities for its use since it can then replace natural gas and be applicable for use in the vehicles. However, upgrading adds to the costs of biogas production. It is, therefore, important to have an optimized upgrading process in terms of low energy consumption and high efficiency giving high methane content in the upgraded gas. Apart from direct combustion in burners or boiler units, gas engines are usually employed as prime movers in the utilization of biogas [16–18]. There is even greater potential for biogas if it can be compressed for using in farm machinery. But all these scopes are possible only after removing CO_2 H_2S and water vapour from crude biogas. As the energy content of biogas is in direct proportion to the methane concentration, therefore, it is necessary to remove these contaminants from the raw biogas generated in the digesters to increase the energy content. Herein, we report the removal of CO_2, H_2S, and H_2O from raw biogas generated from anaerobic codigestion of cattle manure (CM) with cafeteria waste (CW), fruit waste (FW), and vegetable waste (VW).

We used calcium oxide (CaO), iron oxide (Fe_2O_3), zero valent iron (Fe^o), iron chloride ($FeCl_2$), activated carbon, silica gel, and sodium sulfate (Na_2SO_4) for the removal of CO_2, H_2S, and H_2O. The effect of pH was observed for the purification methods. The aim of the study is to optimize the purification process in terms of saving energy consumption and high performance efficiency giving high methane concentration in the purified gas. We propose that the results of the experimental work are used in the design of a biogas treatment system especially in the farm sectors.

2. Methods

2.1. Anaerobic Metabolism Apparatus (Digester).
A "biogas digester" is a simple system which produces usable fuel (biogas) energy, via the natural decomposition of organic material in anaerobic conditions. A laboratory scale cylindrical shape batch type digester is made of $0.2\,m^3$ polypropylene tank (used as a reactor). The tank is airtight using rubber gasket and is clearly placed above the ground level for biogas generation. The cylindrical shape was adopted to enhance better mixing.

2.2. Preparation of Fermentation Substrates.
The digestion feedstocks, namely, cafeteria waste (CW), vegetable waste (VW), and fruit waste (FW), were collected from Kumamoto University and Kokai vegetable market, Kumamoto, Japan. The cattle manure (CM) was collected from the dairy farm, Fukuoka, Japan. Then all substrates were crushed into small pieces of 2 mm sizes with mechanical blender except

CM. The blended sample was mixed with equal proportion $CW : VW : FW : CM$ $(1:1:1:1)$ and diluted with tap water in a ratio of $1:1$. The prepared feedstock was fed by a volume of $0.16\,m^3$ in the biogas digester.

2.3. Absorption and Adsorption Materials.
In the laboratory study, all chemicals were reagent grade or above and used without further purification. The purification materials were used divided into five different mixtures shown in Table 1. All purification reagents were derived from Kanto Chemical Co., Ltd., Japan. Calcium oxide (CaO) and silica gel were crushed manually into powder form to increase the internal surface area.

2.4. Procedure of the Experiment.
The experiments have been carried out in laboratory scale set-up schematically as shown in Figure 1. The set-up consists of three sections: a metabolism section to generate the desired biogas, a contaminants removal section to purify the biogas, and an analysis section. During the study, the experiment was operated batchwise with respect to absorption and adsorption phase. The first section (1) is digester as previously described. The second (2) section is raw gas collection chamber, purification, and the raw biogas sampling section. And the third (3) section is the purified biogas sampling bag. The purification unit consists of three glass flasks ($0.002\,m^3$). We also changed CaO to $Ca(OH)_2$ to obtain positive results. The first flask contains $Ca(OH)_2$ solution which was varied from 1 to 10 g per liter of water for all the experimental runs. The raw gas collection flask and first purification flask were interconnected by 5 mm diameter 0.4 m long hose pipe. Under batch mode conditions, the raw biogas is introduced by 5 mm in diameter, 0.3 m long glass tubing at 0.3 mm above from the bottom of the absorber flask as small bubbles through the $Ca(OH)_2$ $Ca(OH)_2$ solution to remove CO_2, in all runs.

For the adsorption of contaminants (H_2S and H_2O), the first, second, and third removal flask was interconnected by 5 mm diameter and 1 m long U-shaped hose pipe. For the absorption of H_2S, the first and second were interconnected by 5 mm diameter hose pipe on the top of the flasks along two 5 mm in diameter, 0.3 m long glass tubing at 0.3 mm above from the bottom of the H_2S absorption flask as small bubbles through the H_2S removal solutions, in runs R1, R2, R3, and R4, respectively. On the other hand, removal of H_2S hose pipe was filled with activated carbon and for run 5 (R5). The contaminate biogas enters the H_2S adsorption column after passing the CO_2 capture trap through the activated carbon to remove H_2S. Herein notice that when gas was transferred from CO_2 flask to H_2S removal flask, the first and second flask U-shaped connected line was closed by using gas flow control valve in runs R1, R2, R3, and R4 and vice versa for run 5, the glass tubing line was closed.

Similarly, the removal of H_2O the U-shaped adsorption hose column was filled with a freshly prepared powder and granular form of silica gel and sodium sulfate for runs R1, R3 and R4, and R2 and R5, respectively. The biogas enters the moisture eliminate column after passing the H_2S removal unit to ensure that the biogas was dry. As silica gel, Na_2SO_4, and activated carbon materials have significant water and H_2S
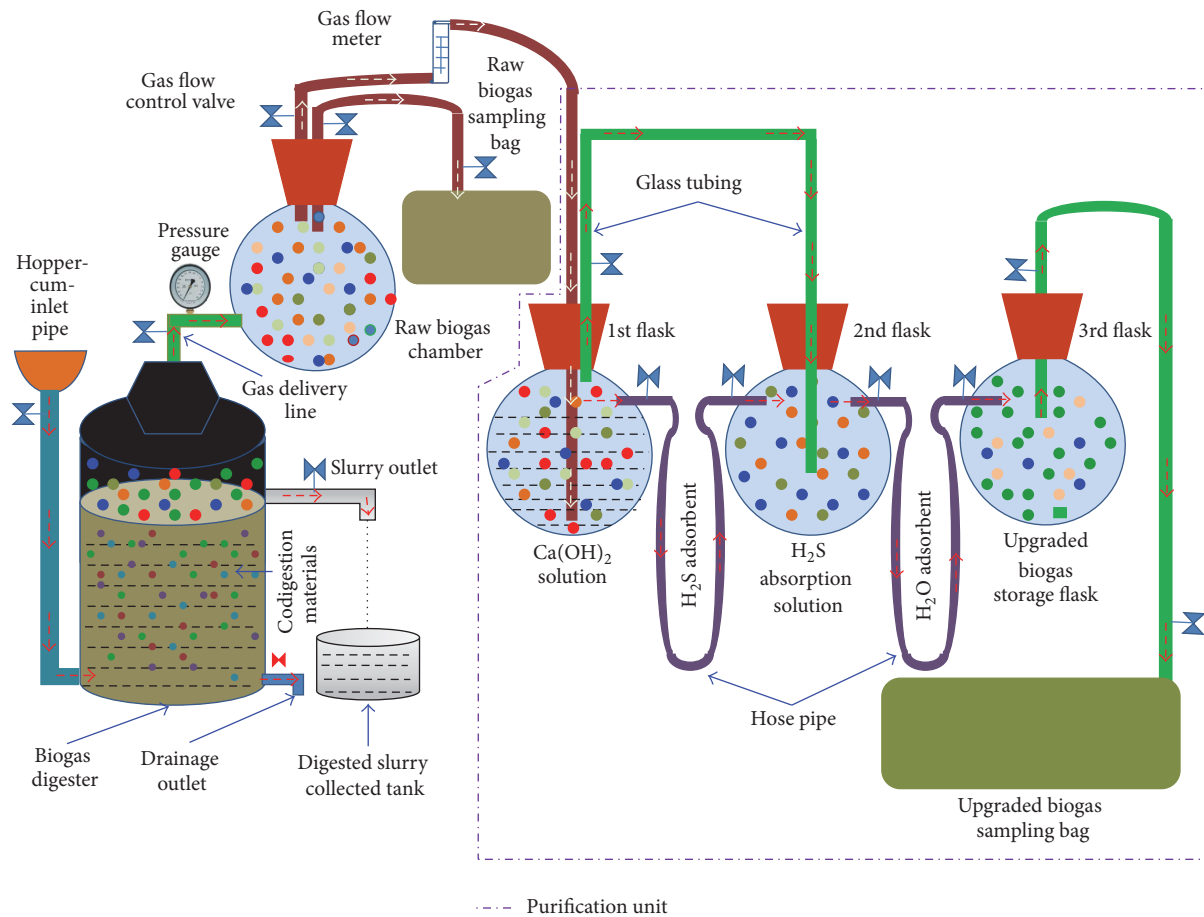
FIGURE 1: Schematic of experimental apparatus set-up for purification of biogas.

TABLE 1: Experimental properties of methane enhancement research work.

Run	Removal mixture	Uploaded water (l)	Chemical substances quantity (g)	Range of pH	pH modulates	Time per exp. (Min.)
	CaO	1		—		
R1	Fe_2O_3	1	1–10	5–9.5	HCl/NH_3	60
	Silica gel	—		—		
	CaO	1		—		
R2	Fe^o	1	1–10	5–9.5	HCl/NH_3	60
	Na_2SO_4	—		—		
	CaO	1		—		
R3	$FeCl_2$	1	1–10	5–9.5	HCl/NH_3	60
	Silica gel	—		—		
	CaO	1		—		
R4	Fe^o	1	1–10	—	—	60
	Silica gel	—		—		
	CaO	1		—		
R5	Activated carbon	—	1–10	—	—	60
	Na_2SO_4	—		—		

adsorbing capability, therefore, biogas flows through these adsorbents from the one end to the other end of the hose. In this regard, both ends of the hose pipe column were attached by soft cotton to increase adsorbing ability. At the end of experiment, purified methane-rich biogas comes out on the top of the flask with CO_2, H_2S, and H_2O being stripped off. Then the purified gas is accumulated in a $0.05 \, m^3$ aluminum gas sampling bag for analyzing gas compositions. Biogas samples were collected before and after it flowed through these media and CH_4 enriched content and the capturing

efficiency was investigated as the percentage of CO_2, H_2S, and H_2O removed from the biogas of each sample. The design consideration was that there were to be no energy requirements for the system operation.

2.5. Sample Measurement Methods. Gas composition was analyzed off line by gas chromatography (GC-8AIT/C159 R8A SHIMADZU Corporation, Japan) and Testo-350 portable gas analyzer (Testo AG, Germany). The gas chromatograph (GC) was fitted with a Porapak N 80/100, 274.32 cm, 1/8 mesh 250 × 250 × 145 mm column, a molecular sieve (mole sieve 5A 60/80, 182.88 cm, 1/8), maximum temperature 399°C, temperature stability ± 0.1°C a stainless-steel column, and a thermal conductivity detector. Detector type was TCD made by tungsten rhenium filament. Maximum temperature and sensitivity of the detector were 400°C and 7000 (mVmL/mg), respectively. Argon (Ar) was used as the carrier gas at a flow rate of 30 mL/min. The column temperature was 60°C and the injector/detector temperatures were 80°C and current 60 (mA). Methane, CO_2, H_2S, and H_2O content of raw biogas and purified biogas were analyzed and compared. The rate of gas flow, pressure, pH, and water content were measured using gas flow meter, pressure gauge, digital pH meter (HM-25R), and moisture meter (MOC63u), respectively.

3. Results and Discussion

3.1. Absorption of CO_2. It refers to the process by which one element, such as a solid or liquid, takes up another element, such as a liquid or gas, through minute pores or spaces between its molecules. The absorption capability of the absorber depends on the equilibrium concentrations between liquid phase and gaseous phase. In this study, CaO solution was used as a chemical solvent to demonstrate the ability to absorb CO_2 from the gas stream. It is an effective method to remove H_2S along with CO_2 from biogas. The calcium oxide (slaked lime) solution is used to promote the chemical reactions:
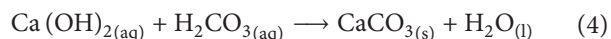
$$CO_{2(g)} + H_2O_{(l)} \longrightarrow H_2CO_{3(aq)} \tag{1}$$

$$CaO_{(s)} + H_2CO_{3(aq)} \longrightarrow CaCO_{3(s)} + H_2O_{(l)} \tag{2}$$

$$CaO + H_2O \longrightarrow Ca(OH)_{2(aq)} \tag{3}$$

$$Ca(OH)_{2(aq)} + H_2CO_{3(aq)} \longrightarrow CaCO_{3(s)} + H_2O_{(l)} \tag{4}$$
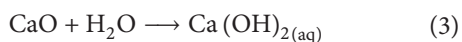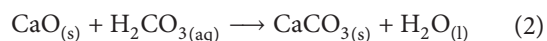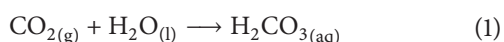
Figure 2 shows the inflow versus outflow CO_2-concentration of biogas for all experiments after treating with 1–10 g of CaO solution. During the experimentation phase, the CO_2-concentration of the biogas inflow varied from a minimum of 33%, 34%, 36%, 35%, and 34% to 37%, 38%, 40%, 40%, and 38% for the runs R1, R2, R3, R4, and R5, respectively. The CO_2-concentration of biogas decreased from approximately 25%, 28%, 29%, 26%, and 24% to 5%, 5.8%, 5.8%, 5.9%, and 3% at 1 to 10 g of CaO in R1, R2, R3, R4, and R5, respectively. We observed that the run (R5) of CO_2 concentration decreased significantly higher than other runs. It is because CO_2 is also absorbed when passing through the
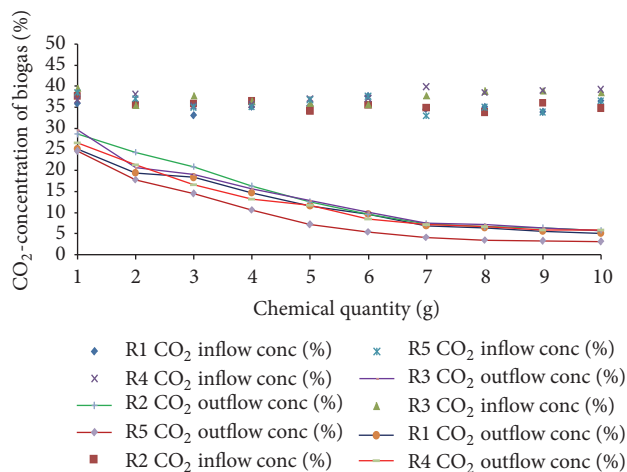

FIGURE 2: CO_2 inflow versus outflow concentration of biogas under the treatments of runs R1, R2, R3, R4, and R5.

activated carbon and silica gel during the study. It is noticeable that the concentration of CO_2 decreased sharply in all experiments up to 6 g of CaO solution and the decreasing trends almost remained stable at 7 to 10 g.

3.2. Absorption and Adsorption of Hydrogen Sulfide (H_2S). To characterize the chemical reagents some experiments were performed using the absorption of H_2S in an $Fe_2O_3/Fe^o/FeCl_2$ solution. The pH value of the phase was modulated by HCl and NH_3 solution for runs R1, R2, and R3. The NH_3 solution was chosen because the reaction of H_2S and a NH_4OH solution is instantaneous with respect to mass transfer and the absorption of H_2S is therefore gas phase mass transfer controlled if the concentration of the NH_3 concentration is sufficiently high [19]. The experimental data are presented in Figure 3(a). From Figure 3(a) it can be seen that, at a pH higher than 9, the conversion of H_2S was more or less independent of the pH and the initial concentration of H_2S in the gas. When the pH dropped below 7 the removal of H_2S concentration decreased significantly in R1 and R3. The absorption of H_2S in $Fe_2O_3/FeCl_2$ solutions has been studied as a function of the pH of the solution and the concentration of H_2S in the gas entering the reactor. At the start of an experiment, the pH was brought to a value of approximately 5 by adding some HCl. At a pH of approximately 5, the H_2S uptake of the solution decreased slightly and a small amount of NH_3 was added to bring the pH of the solution 0.5 intervals from 5 to 9.5. Then a gas stream with a different concentration of H_2S was brought in contact with the solution and the experiment was continued. Using this procedure the average concentration of H_2S in the gas entering the reactor was varied between 478 ppm and 492 ppm and 480 ppm and 512 ppm for R1 and R3, respectively. From the experimental results obtained with the solutions it can be concluded that it is possible to decrease 50 ppm and 69 ppm of the H_2S from a gas stream that initially contains between 478 ppm and 492 ppm and 480 ppm and 512 ppm H_2S for R1 and R3 respectively, when the pH of the solution is 9.5. With the pH below 7 the removal of H_2S appeared to be lower. This might
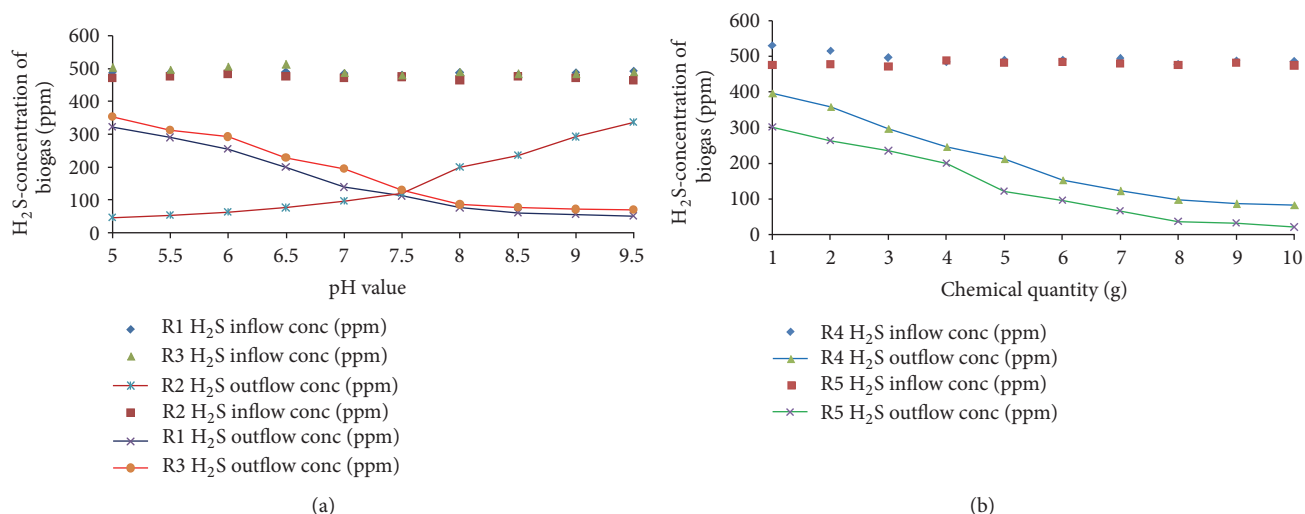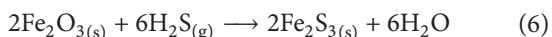
(a)

(b)

FIGURE 3: (a) H_2S inflow versus outflow concentration of biogas under the treatments of runs R1, R2, and R3 and (b) for runs R4 and R5.

be caused that the absorption of H_2S was not (completely) gas phase mass transfer limited but also partly influenced by precipitation and/or liquid phase mass transfer. However, the results show that a virtually low desulfurization should be possible at pH values as low as 5.5. The chemical reactions that take place with the H_2S, $FeCl_2$, and Fe_2O_3 are as follows:

$$FeCl_2 + H_2S \longrightarrow FeS \downarrow + 2HCl \qquad (5)$$

$$2Fe_2O_{3(s)} + 6H_2S_{(g)} \longrightarrow 2Fe_2S_{3(s)} + 6H_2O \qquad (6)$$

The reaction is slightly endothermic: a temperature minimum of about 12°C is required to provide the necessary energy. The iron oxide can be regenerated with oxygen according to the following reaction:

$$2Fe_2S_3 + 3O_2 \longrightarrow 2Fe_2O_3 + 6S \qquad (7)$$
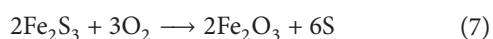
This reaction is exothermic and therefore a large amount of heat is released during regeneration process [15].

On the other hand, for R2, Fe^o represented a nanotechnology material providing high surface areas, developing a nanoscale absorbent with high absorption capacity becoming promising for H_2S removal [20, 21]. Herein we investigated the effectiveness of Fe^o for sulfide removal with respect to pH conditions range which varied 5–9.5 illustrated in Figure 3(a). From R2, it can be seen that, at a pH higher than 9, the conversion of H_2S was less which are reversed behavior compared to R1 and R3. The average sulfide concentration was passed about 471 ppm through Fe^o solution. Approximately 426 ppm of sulfide concentration was removed at pH 5 in R2 and comes to 45 ppm. However, the sulfide removal concentration decreased as pH increased. In this study, we observed that the oxidation of Fe^o leading to the generation of Fe(II) is favorable under acidic conditions:

$$Fe^o_{(s)} + 2H_2O \longrightarrow Fe^{2+} + H_{2(g)} + 2OH^- \qquad (8)$$
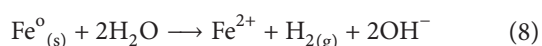
Sulfide readily reacted with Fe(II) to form iron sulfide (FeS) [22, 23]:

$$Fe^{2+} + H_2S \longrightarrow FeS + 2H^+ \qquad (9)$$

$$Fe^{2+} + HS^- \longrightarrow FeS + H^+ \qquad (10)$$
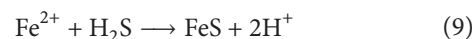
Accordingly, the pH effect on the sulfide removal with Fe^o may be attributed to the formation of FeS through the precipitation of Fe(II) and sulfide.

Similarly, for an aqueous Fe^o solution the H_2S conversion was also measured for various inflow H_2S concentrations and as a function of the mass in the solution as shown in Figure 3(b). The quantity of Fe^o increased gradually in the solution up to 10 g. At 10 g the H_2S concentration became lower than 85 ppm and the experiment was stopped. A number of experiments were performed with H_2S concentrations in the gas entering the reactor varying between 475 ppm and 530 ppm for run R4. When the experimental results are compared, it can be seen that aqueous Fe^o solutions behave slightly lower than Fe^o solutions with pH study with respect to the absorption of H_2S. However, it appeared, for example, to be possible to remove more than 412 ppm of H_2S from a gas stream that on average contained 494 ppm of H_2S at 10 g of Fe^o. It can be seen that a substantial decreasing trend remained almost stable in H_2S concentration, between the quantities 8 to 10 g.

Finally, the selected activated carbon was tested along with the variable mass of H_2S removing phase (activated carbon). As shown in Figure 3(b), the average H_2S-concentration was varied 473 ppm and 487 ppm introduced into the run (R5); after adsorption, this concentration gradually decreased based on the amount by up to 20 ppm when 10 g activated carbon is used.

The H_2S-concentration was changed from 301 ppm to 20 ppm at 1 and 10 g activated carbon, respectively. We observed that the adsorbing capacities depend on the degree of saturation and the mass of adsorbing substance. In this case, the activated carbon removed more H_2S than other runs

due to its extremely porous form of carbon and thus it has a very large surface area available for adsorption [24]. It also shows strong affinity to polar substances such as H_2O, H_2S, CO_2, and SO_2. In this case of H_2S, activated carbon adsorbs and decomposes it to elemental sulfur.

3.3. Adsorption of Water Vapour (H_2O).

It refers to the process by which molecules of a substance, such as a gas or a liquid, collect on the surface of a solid. The objective of this experiment was to investigate that H_2O can be efficiently removed from a biogas stream. Because biogas from digesters is normally collected from headspace above a liquid surface or very moist substrate, the gas is usually saturated with water stream. The amount of saturated water vapour in a gas depends on temperature and pressure. Biogas typically contains 10% water vapour by volume at 43°C, 5% by volume at 32°C, and 1% by volume at 4.5°C [25]. The removal of water vapour (moisture) from biogas reduces corrosion that results when the H_2S and CO_2 have not been removed from the biogas because the H_2S and CO_2 and water vapour react to form different acids, which can result in a severe risk factor in equipment that comes into contact with the biogas. In addition, water vapour condenses within a system due to pressure or temperature changes; it can result in clogging of the pipes. The adsorption process was carried out at different mass of adsorbent substances in the range from 1 to 10 g. Figure 4 represents the change in H_2O-concentration in raw and purified biogas for the all experimental runs. During the operation the concentration of H_2O of the gas was monitored entering and leaving the reactor. When the mass of silica gel is 1 g the removal media were capable of decreasing the H_2O-concentration in the gas with approximately 1.7%, 1.6%, and 1.5% in runs R1, R3, and R4, respectively. When the silica gel quantity of the removing reactor increased until 10 g, the degree of removal increased considerably. The colour of the silica gel was changed from blue to pink after absorbing water vapour from the raw biogas. The reason is that silica gel is extremely porous and can adsorb a large amount of water due to its large internal surface area. However, the H_2O-concentration in the purified biogas at the end of the experiment was contained 0.25%, 0.24%, and 0.21% for runs R1, R3, and R4, respectively. The results show that the removal of H_2O-concentration almost remained stable at 8 to 10 g of silica gel. The silica gel was reactivated after saturation by heating it in an oven at 150°C for 3 hours to remove the adsorbed H_2O.

To demonstrate the adsorption of H_2O from biogas by treating Na_2SO_4 substance on lab scale reactor plants, Figure 4 represents also the removal of H_2O of the biogas entering and leaving the reactor which was investigated using Na_2SO_4 as an adsorbent. From this figure, it can be seen that when the Na_2SO_4 quantity in the adsorption column is significantly high (10 g), the Na_2SO_4 substance is capable of decreasing the H_2O concentration in the gas by approximately 4% and 5.5% from 4.8% and 5.9% in runs R2 and R5, respectively. The results showed that the concentration of H_2O in the biogas stream leaving the adsorber was approximately 0.7% and 0.3% at 10 g of Na_2SO_4 in runs R2 and R5, respectively. It can be seen that the run R2
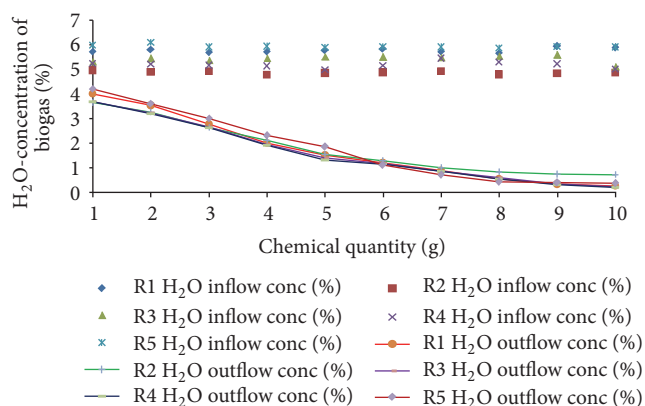

FIGURE 4: H_2O inflow versus outflow concentration of biogas under the treatments of runs R1, R2, R3, R4, and R5.

adsorption capacity is significantly lower than R5. The exact reason is that in R5 the activated carbon also adsorbed some water molecules before entering moisture trapped column of Na_2SO_4. We also investigated the H_2O concentration that remained almost stable at 8 to 10 g of Na_2SO_4 and then the experiment was stopped.

3.4. Comparative Removal Efficiency of the Study Runs R1, R2, and R3.

Figure 5(a) shows the results obtained in terms of CO_2, H_2S, and H_2O removing efficiencies as function of mass and pH. First, we made a comparative analysis of the different research stages. It shows the different types of removal substances for runs R1 and R3 with almost similar results of CO_2 and H_2O removing phase, whereas R1 and R2 present similar results of H_2S removing phase. But for a run (R2) maximum removal efficiency was observed at low pH, whereas R1 maximum efficiency was obtained at high pH. The reason is that the oxidation of Fe^o leading to generation of $Fe(II)$ is favorable under acidic conditions and Fe_2O_3 favorable under base conditions In case of R1 and R3 results showed that the CO_2 and H_2O removal efficiency was similar due to the same material used. However, the R1, R2, and R3 are able to reach $H_2S > 89\%$, 90%, and 85% (final H_2S = 50 ppm, 45 ppm, and 69 ppm) for 10 g when pH = 9.5, 5, and 9.5. Under these circumstances removal efficiency of $CO_2 > 85\%$, 83%, and 84% (final $CO_2 < 6\%$) and $H_2O > 95\%$, 85%, 95% (final $CO_2 < 0.2\%$, 0.7%, and 0.2%) for 10 g, respectively. It can be seen that the removal efficiency of H_2O for R2 is a little bit lower due to hard granular form (Na_2SO_4) results that lower adsorption capacity. This result shows that the best removal efficiency was achieved in R1, although there were not so significant differences of performance compared with other contaminants elimination methods.

3.5. Comparative Removal Efficiency of the Study between Runs R4 and R5.

The contaminants of biogas removal efficiency for runs R4 and R5 increased during the experimental period as shown in Figure 5(b). The results showed that the most efficient performance in R5 was investigated to compare between runs R4 and R5. The operation of the system in runs R4 and R5 was very similar with slightly better results in run
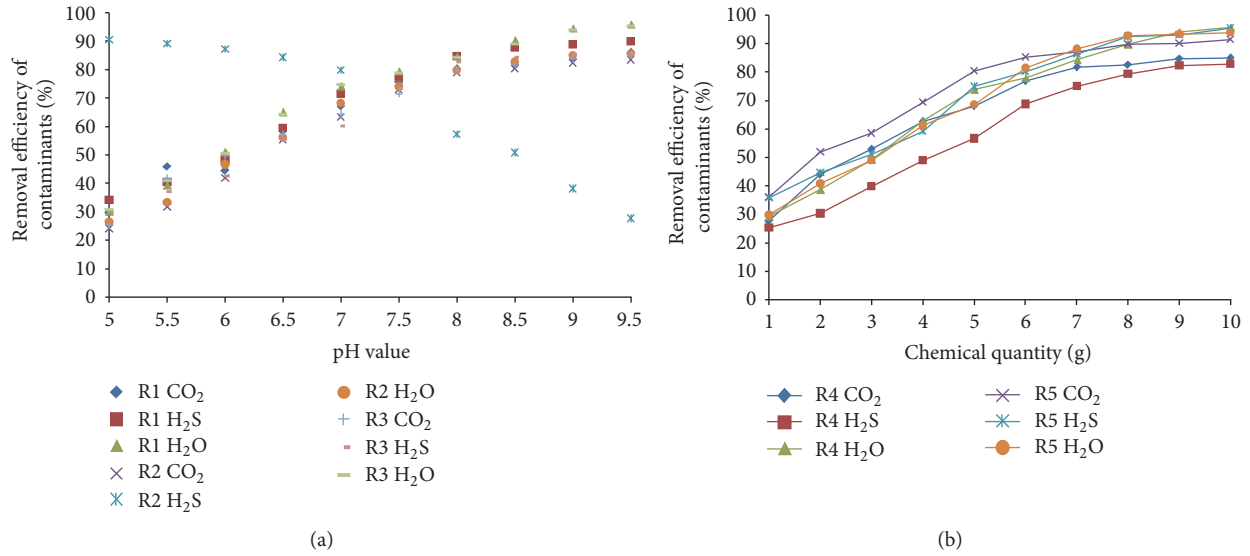
FIGURE 5: (a) CO_2, H_2S, and H_2O removal efficiency of biogas under the treatments of runs R1, R2, and R3 and (b) for runs R4 and R5.
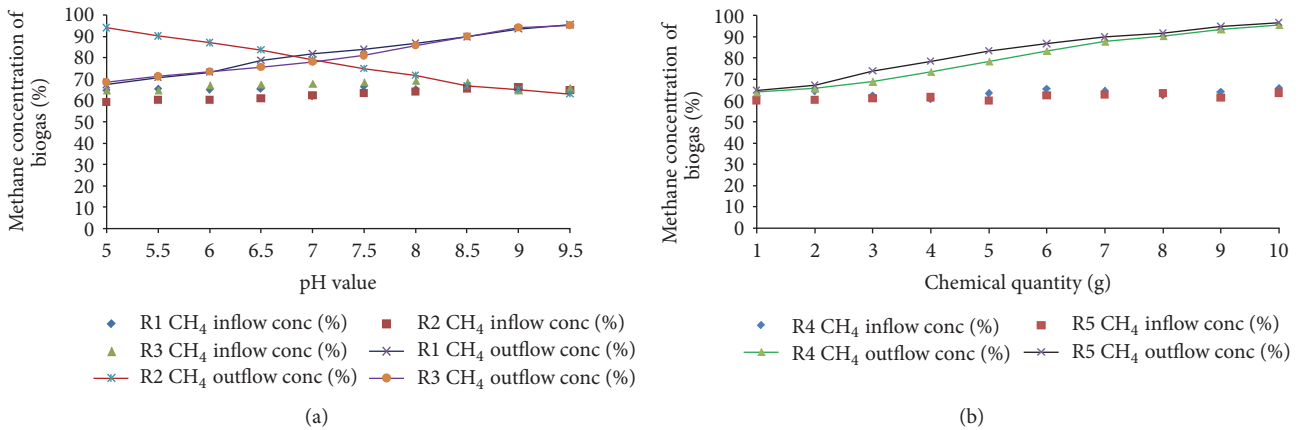

FIGURE 6: (a) CH_4 inflow versus outflow concentration of biogas under the treatments of runs R1, R2, and R3 and (b) for runs R4 and R5.

R5 with respect to H_2O removal efficiency. It can be seen that the elimination performance is significantly lower in R4 than R5 regarding CO_2 and H_2S elimination. A possible reason for this was that run R5 contained activated carbon, which is extremely porous and thus has a very large surface area for adsorption of H_2S and simultaneously CO_2. However, runs R4 and R5 are able to achieve removal efficiency of $H_2S > 82\%$ and 95% (final $H_2S = 82$ ppm and 20 ppm) at 10 g. Regarding these conditions the removal efficiency of $CO_2 > 84\%$ and 91% (final $CO_2 < 6\%$ and 4%) and $H_2O > 95\%$ and 93% (final $CO_2 < 0.2\%$ and 0.3%) for 10 g, respectively.

The study results obtained reveal that the most efficient runs of the treatment process were in order of R5 > R1 > R4 > R3 > R2. Among all results showed that the removing efficiency with the best performance was R5. We also observed that the Fe^o was more efficient in R2 than R4 for removing of H_2S.

3.6. Comparison of Upgrading Methane Concentration in the Treated Biogas. The concentration of CH_4 increased sharply

over the investigated period with the increasing mass of substances as well as pH value in the removal media of R1 and R3 while CH_4 concentration increased with low pH and high quantity of reagents for R2 as shown in Figure 6(a). However, the maximum CH_4 concentration abilities reach approximately 95%, 94%, and 95% at 10 g for runs R1, R2, and R3, respectively. Figure 6(b) clearly shows that the CH_4 concentration increases favorably with mass of reagents. As far as enrichment of CH_4 concentration in the gas phase is concerned, the highest increase was observed with 10 g removal process, achieved in R4 and R5 (95% and 96%), respectively. For the sake of comparison, the best methane concentration in the feed biogas was achieved in R5 regarding of $CH_4/CO_2/H_2S/H_2O$ mixtures.

The H_2S is removed by Fe_2O_3, Fe^o, and $FeCl_2$ through chemical transformation of H_2S into S. This chemical method is fascinating as it eliminates the pollutant H_2S. The activated carbon removes H_2S by simple adsorption through its mesoporous surface. The water vapour is removed by physical adsorption only. The experimental results revealed that CH_4

is possible to enrich by 95% using the chemical and physical removal process for CO_2, H_2S, and H_2O. Therefore, these processes are feasible to meet the standard for injection of the gas in grid or vehicle fuel [26].

4. Conclusions

We generated biogas from the wastes of cafeteria, vegetable, food, and cattle manure. The source of material used in biogas production has a significant effect on the composition of biogas. The results showed that the CaO solutions are capable of reducing CO_2 concentration below 6%. Removal of H_2S was investigated by treating the raw biogas with $FeCl_2$, Fe^o, Fe_2O_3, and activated carbon. Approximately the H_2S concentration was reduced to 89%, 90%, 86%, 85%, and 96% for treating the raw biogas with pH for 10 g of Fe_2O_3, Fe^o $FeCl_2$, and without pH for Fe^o, and activated carbon for R1, R2, R3, R4, and R5, respectively. Removal of H_2O was investigated by treating the raw biogas with Na_2SO_4 and silica gel. The H_2O concentration was reduced to 0.2%, 0.7%, 0.2%, 0.2%, and 0.3% for treating the raw biogas with 10 g of Na_2SO_4 and silica gel, for R1, R2, R3, R4, and R5, respectively. The conclusions are also confirmed in regard to performance run R5 which is the best purification process. The possibility for the enrichment of above 95% in biogas using combined chemical absorption and adsorption indicates the practical application of this process.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

References

[1] M. R. A. Mamun, M. S. Kabir, M. M. Alam, and M. M. Islam, "Utilization pattern of biomass for rural energy supply in Bangladesh," *International Journal of Sustainable Crop Production*, vol. 4, no. 1, pp. 62–71, 2009.

[2] C. N. Hamelinck, G. Van Hooijdonk, and A. P. C. Faaij, "Ethanol from lignocellulosic biomass: techno-economic performance in short-, middle- and long-term," *Biomass and Bioenergy*, vol. 28, no. 4, pp. 384–410, 2005.

[3] Y. Sun and J. Cheng, "Hydrolysis of lignocellulosic materials for ethanol production: a review," *Bioresource Technology*, vol. 83, no. 1, pp. 1–11, 2002.

[4] M. Pöschl, S. Ward, and P. Owende, "Evaluation of energy efficiency of various biogas production and utilization pathways," *Applied Energy*, vol. 87, no. 11, pp. 3305–3321, 2010.

[5] F. Rossi and A. Nicolini, "A cylindrical small size molten carbonate fuel cell: experimental investigation on materials and improving performance solutions," *Fuel Cells*, vol. 9, no. 2, pp. 170–177, 2009.

[6] F. Cotana, F. Rossi, and A. Nicolini, "A new geometry high performance small power MCFC," *Journal of Fuel Cell Science and Technology*, vol. 1, no. 1, pp. 25–29, 2004.

[7] F. Rossi and A. Nicolini, "Ethanol reforming for supplying molten carbonate fuel cells," *International Journal of Low-Carbon Technologies*, vol. 8, no. 2, pp. 140–145, 2013.

[8] J. Chang, J. Fontenelle, and N. Serveau, "Inventaires des émissions polluantes atmosphériques en France, séries sectorielles et analyses et étendues," Tech. Rep., CITEPA, Paris, France, 2007.

[9] A. Wellinger and A. Lindberg, "Biogas upgrading and utilisation," IEA Bioenergy Task 24: Energy from Biological Conversion of Organic Waste, 2005.

[10] E. Wheless and J. Pierce, "Siloxanes in landfill and digester gas update," Whittier (Canada) and Long Beach (California): Los Angeles Country Sanitation Districts and SCS Energy, 2004.

[11] M. Hagen, E. Polman, J. Jensen, A. Myken, O. Jönsson, and A. Dahl, "Adding gas from biomass to the gas grid," Report SCG 118, Swedish Gas Center, Malmö, Sweden, 2001.

[12] M. Persson and A. Wellinger, "Biogas upgrading to vehicle fuel standards and grid injection," Report, IEA Bioenergy, 2006.

[13] K. Krich, A. Augenstein, J. Batmale, J. Benemann, B. Rutledge, and D. Salour, "Upgrading dairy biogas to biomethane and other fuels," in *Biomethane from Dairy Waste-A Sourcebook for the Production and Use of Renewable Natural Gas in California*, K. Andrews, Ed., pp. 47–69, Clear Concepts, California, Calif, USA, 2005.

[14] T. Bansal, N. Tripathi, and G. Chawla, "Upgradation of biogas using combined method of alkaline water scrubbing and adsorption through carbon molecular sieve," *International Journal of ChemTech Research*, vol. 5, no. 2, pp. 886–890, 2013.

[15] E. Ryckebosch, M. Drouillon, and H. Vervaeren, "Techniques for transformation of biogas to biomethane," *Biomass and Bioenergy*, vol. 35, no. 5, pp. 1633–1645, 2011.

[16] P. Börjesson and B. Mattiasson, "Biogas as a resource-efficient vehicle fuel," *Trends in Biotechnology*, vol. 26, no. 1, pp. 7–13, 2008.

[17] N. Tippayawong, A. Promwungkwa, and P. Rerkkriangkrai, "Long-term operation of a small biogas/diesel dual-fuel engine for on-farm electricity generation," *Biosystems Engineering*, vol. 98, no. 1, pp. 26–32, 2007.

[18] N. Tippayawong, A. Promwungkwa, and P. Rerkkriangkrai, "Durability of a small agricultural engine on biogas/diesel dual fuel operation," *Iranian Journal of Science and Technology, Transaction B: Engineering*, vol. 34, no. 2, pp. 167–177, 2010.

[19] P. V. Danckwerts, *Gas-Liquid Reactions*, McGraw-Hill Book Company, New York, NY, USA, 1970.

[20] X.-Q. Li, D. G. Brown, and W.-X. Zhang, "Stabilization of biosolids with nanoscale zero-valent iron (nZVI)," *Journal of Nanoparticle Research*, vol. 9, no. 2, pp. 233–243, 2007.

[21] W. Yan, A. A. Herzing, C. J. Kiely, and W.-X. Zhang, "Nanoscale zero-valent iron (nZVI): aspects of the core-shell structure and reactions with inorganic species in water," *Journal of Contaminant Hydrology*, vol. 118, no. 3-4, pp. 96–104, 2010.

[22] A. H. Nielsen, P. Lens, J. Vollertsen, and T. Hvitved-Jacobsen, "Sulfide-iron interactions in domestic wastewater from a gravity sewer," *Water Research*, vol. 39, no. 12, pp. 2747–2755, 2005.

[23] D. Rickard and G. W. Luther III, "Chemistry of iron sulfides," *Chemical Reviews*, vol. 107, no. 2, pp. 514–562, 2007.

[24] M. S. Horikawa, F. Rossi, M. L. Gimenes, C. M. M. Costa, and M. G. C. Da Silva, "Chemical absorption of H_2S for biogas purification," *Brazilian Journal of Chemical Engineering*, vol. 21, no. 3, pp. 415–422, 2004.

[25] R. Weast and I. Hodgeman, *Handbook of Chemistry and Physics*, CRC Publishing, Boca Raton, Fla, USA, 1958.

[26] M. Persson, "Utvä rdering av uppgraderingstekniker för biogas," Rapport SGC 142, Svenskt Gastekniskt Center, Malmö, Sweden, 2003.

Journal of
Engineering

The Scientific
World Journal

International Journal of
Rotating
Machinery

Journal of
Sensors

International Journal of
Distributed
Sensor Networks

Advances in
Civil Engineering

Journal of
Control Science
and Engineering

Journal of
Robotics

Journal of
Electrical and Computer
Engineering

Advances in
OptoElectronics

VLSI Design

International Journal of
Navigation and
Observation

Modelling &
Simulation
in Engineering

International Journal of
Aerospace
Engineering

International Journal of
Chemical Engineering

International Journal of
Antennas and
Propagation

Active and Passive
Electronic Components

Shock and Vibration

Advances in
Acoustics and Vibration

Hindawi

Submit your manuscripts at
https://www.hindawi.com