Hydrogen Sulphide Removal from Biogas: A Review of The Upgrading Techniques and Mechanisms Involved

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Abstract- The production of biogas through anaerobic digestion may play an important role in the economy due to the possibility to produce renewable energy from organic waste material. Biogas is considered as a clean form of energy but unfortunately it contains impurities such as hydrogen sulphide (H_2S) which makes it ineffective for heating and lighting hence, its removal in biogas upgrading to biomethane is crucial. Due to its corrosive nature and contribution to the greenhouse gas emissions, innovation and efficient strategies for H_2S removal are required so that the quality of biogas can be improved for sustainability and economic growth. The removal of H_2S is important as far as biogas upgrading is concerned so as to prevent operational hazards and protect the environment, hence the strategies for its removal for effective and eco-friendly use of biogas are the focus of this review. Review papers with both detailed mechanisms and different methods for H_2S removal from biogas are lacking. The understanding of the mechanisms that are involved in H_2S removal in each method is important hence the review also presents and discusses insightful mechanisms proposed by different researchers. Based on the mechanisms presented in this review, it can be concluded that it is very possible to design and build efficient biogas upgrading plants and also develop cost effective materials with a high removal efficiency.

Keywords Biogas, digesters, anaerobic digestion, hydrogen sulphide removal, mechanisms.

1. Introduction

Biogas production from organic waste such as agricultural, animal and human waste through anaerobic digestion is essential as it is part of a sustainable energy system [1]. Since biogas is renewable, it can replace fossil fuels in producing power and heat. Large scale production of biogas has been on the increase since it can also be used as a gaseous vehicle fuel. The use of biogas contributes significantly to lowering the greenhouse gas concentration when properly packed and not allowed to escape into the atmosphere [2]. It has been reported that the world primary energy consumption between 2002 and 2030 is mainly fossil fuels which has a negative impact on the environment due to CO_2 emmissions [3]. The fossil fuels are getting depleted hence the use of renewable energy seem to be analternative [4]. It has been estimated that the use of biogas is going to

double in future, an increase from 14.5 GW in the year 2012 to about 29.5 GW this year, 2022 [5].

The use of biogas is hampered by trace compounds such as hydrogen sulphide (H_2S) which causes corrosion to internal combustion engines making repairs expensive and may cause service interruptions [6,7]. H_2S is an extremely toxic gas with an unpleasant odour and is one of the most harmful pollutants that is found in fuels and chemicals such as landfill gas, natural gas, refinery gas, tail gas and biogas. It can result in very serious health risks. Table 1 shows the properties of hydrogen sulphide both physical and chemical.

H_2S is formed from bacteria that is capable of reducing sulphates in the digester. This unpleasant gas can be formed as well from the degradation and digestion of compounds containing sulphur and proteins such as methionine and cysteine present in material fed into the digester. Its production range is dependent upon two components namely,

the amount of the available sulphur (S) containing compounds in the sludge as well as S reducing microorganisms and methanogens which compete for the same substrates [8,9,10]. It has been reported that, high levels of H_2S are found in biogas produced from manure and feedstock rich in protein [11]. H_2S generation can be reduced by appropriate conditioning of the sewage sludge [12]. Besides the most common H_2S, there are other compounds that contain sulphur that might be also present in raw biogas.

Table 1: Physical and chemical properties of H_2S [13].

Property	Value
Relative molecular mass	34.08 g/mol
Density	1.363 g/dm^3
Boiling point	−60.25 °C
Melting point	−82 °C
Critical temperature	100.25 °C
Dipole moment	0.97 D
Critical pressure	89.7 bar
Solubility in H_2O at 20 °C	4 g/dm^3
Acidity	7 pKa

The concentration of H_2S in biogas ranges from between 10-30 ppm to 1000-2000 ppm. It has been reported that continuous exposure to H_2S at levels in the range 15-50 ppm, results in irritation of mucous membranes, headaches, dizziness, and nausea. On the other hand, exposure to high levels of 200-300 ppm, may cause respiratory problems resulting in a coma and/or even unconsciousness [14]. Environmental regulations limit the levels of H_2S in transportation fuels and its concentrations should meet the specifications of where it is going to be used. Its removal or reduction to permissible levels before transportation or use is needed since it causes corrosion in pipelines during transportation and may poison catalysts even at low concentrations. Its removal will also give better performances in the processes that make use of biogas. In fuel cells, if H_2S is not removed, it can react with a nickel catalyst leading to the degradation of the electrolyte and reduced half-life of the cell. In molten carbonate fuel cells, the presence of poisons in biogas for instance, S and chloride containing compounds causes deterioration and short life span of the cell due to the chemical reaction with nickel catalyst and electrolyte [15,16].

Biogas quality is influenced by pre-treatment of the organic feedstocks and the anaerobic digestion operation temperature [17]. The composition of biogas also depends on the pH in the reactor and the nature of the substrate but generally the composition is normally in the ranges CH_4 (35–75%), CO_2 (25–65%), hydrogen (1-5%), nitrogen (0.3–3%) and some small amounts of H_2S, water vapour, ammonia, halides, mercaptans and siloxanes [17,18]. The components quantity and percentages heavily depend on the source of raw

materials and its treatment which will in turn determine the resulting biogas quality, economic value, and the amounts of hazardous secondary pollutants produced by the use of raw biogas.

To enhance the value of biogas, it has to be purified and upgraded. According to Mulu et al., 2021, biogas purification is whereby trace contaminants such as H_2S, water, O_2, NH_3, N_2 and siloxanes are removed whereas biogas upgrading involves the removal of CO_2 [19]. Carbon dioxide removal results in an increase in the concentration of methane. Purified biogas has more than 90 % methane and has better calorific value than the raw biogas which makes it suitable for use as a green renewable fuel. It has a thermal heating value that lies between 15 and 30 MJm^{-3} which is quite similar to that of natural gas hence when upgraded, it is equivalent to natural gas which is why a lot of research on biogas upgrading has been conducted. Although a lot of reviews have been done on biogas purification, the advanced review of the removal of hydrogen sulphide and mechanisms involved its removal has received less attention. In this review, the removal of H_2S using different methods and the proposed mechanisms of its removal is given where possible and this makes this review unique. This review is a contribution to knowledge for upcoming researchers working on biogas purification to get as much information as possible particularly the mechanisms involved in each chosen method. The mechanisms presented in this review can help in designing biogas upgrading plants and also develop cost effective materials with high removal efficiency.

2. H_2S Removal Techniques

In order to have a high energy content, it is highly recommended that before the biogas can be used, it should be upgraded. Although a lot of work has been done to come up with H_2S tolerant materials for catalytic use of biogas to reduce its levels to 10-100 ppm, it is still a major priority to completely remove H_2S [17]. Deublein & Steinhauser., 2007 reported that the maximum concentration of H_2S permissible in biogas used for combined heat and power generation should be in the range 100-500 mg/Nm^3 [20]. When it is used as a fuel for vehicles, the concentrations will depend on the vehicle manufacturer, but generally it should be less than 5 mg/Nm^3 [20].

Several methods are available for the removal of H_2S (Fig. 1), and these include biological treatment, adsorption, and scrubbing. Each method has its own advantages and disadvantages. Hydrogen sulphide can either be eliminated in the digester or after the digester but in some upgrading techniques, it is important to remove it before upgrading to avoid the undesirable effects it has on the plant such as binding irreversibly on the adsorption material. It is important to note that H_2S removal in some upgrading techniques is easier because it is highly soluble in water.
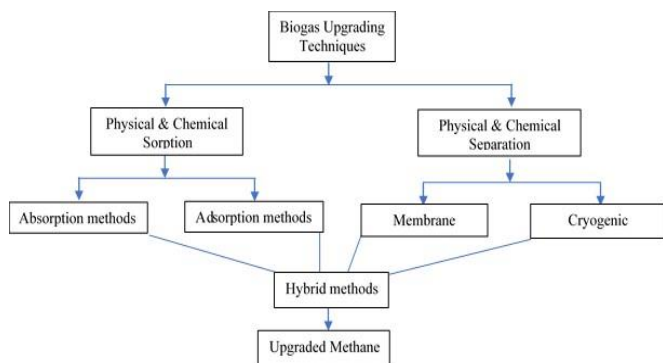
Fig. 1: Different methods for biogas upgrading [21].

Most of the available methods to get rid of H_2S are chemically based and they are quite costly although other methods such as physical and/or biological treatments can be used. H_2S removal using chemical processes is costly because of the high chemical and energy needs, and also disposal costs [22]. This strongly affects the finances related to potential revenues from energy produced from the plant. For these reasons, biological treatment methods become desirable. Biological processes have been found to have a potential to overcome most of the challenges found in chemical processes (Kim et al. 2002). Adsorption on solids with high surface areas, scrubbing or washing with liquid solvents, cryogenic separation, biofiltration, membrane separation, Claus process and chemical oxidation are some of the methods for H_2S removal [23].

The regulation for H_2S is stricter when compared to other impurities but by virtue of its small quantities, the cost of its removal is minimal. Therefore, the method selected for its removal is determined by the demand and to some extent by other factors such as, end use of biogas, availability, operating costs, and maintenance costs. The commonly used methods in biogas industry for H_2S removal are shown in Table 2.

Table 2: H_2S removal technology, capability, and cost per kg [24,25,26,27].

Technology	Ability	Cost/kg H_2S
Iron hydroxide or oxide	< 1.0ppm	ND
Sodium hydroxide scrubbing	1.0ppm	ND
Biological desulphurisation	<50ppm	0.1–0.25 EUR
Impregnated activated carbon	<0.1 ppm	3.85 EUR
Iron chloride	100–150 ppm	0.85 EUR
Metal ion in an aqueous solution	1.0 ppm	

ND: Not determined

2.1 Removal by adsorption

Adsorption also known as chemisorption is a process that involves attraction of the adsorbate on the adsorbent. The advantages of this method include:

(i)   it is relatively cheap,

(ii)   it is simple,

(iii)   high adsorption capacity and

(iv)   possibility of high regeneration degree.

Its disadvantages include, non-selectivity which results in adsorption of other impurities, loss of adsorbent during regeneration, and loss of adsorption capacity after regeneration. A good adsorbent for H_2S removal is one that has good sulphur loading capacity, easy to regenerate and has a structure that is stable. In order to reduce the operating costs, the chosen adsorbent should be easy to regenerate because from an industrial point of view, it is a concern to minimize waste production which needs disposal.

2.1.1 Types of Adsorbents

2.1.1.1 Zeolites

According to Ozekmekci et al., 2015, there are one hundred and ninety-four zeolite frameworks and more than forty naturally occurring zeolites [28]. Some examples of zeolites and their chemical structures include:

(i)   13X ($5Na_2O \cdot 5Al_2O_3 \cdot 14SiO_2 \cdot XH_2O$),

(ii) 5A ($0.7CaO \cdot 0.3Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 4.5H_2O$),

(iii) 4A ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot XH_2O$),

(iv) WE-G 592 (sodium alumina-silicates sodium form of type X crystal structure) and

(v) APG-II ($Na_x[(AlO_2)_x \cdot (SiO_2)_y] \cdot zH_2O$ sodium form of type X molecular sieve [29].

Zeolites are known to be effective in the removal of water and H_2S. Natural zeolites need to be activated first using metals or their oxides before they can be used to increase their adsorption capacity. When used in commercial separation, they show better properties than synthetic zeolites [28]. It was also reported that their adsorption capacity for H_2S is high than that of synthetic zeolites and regeneration is easy resulting in low costs [28].
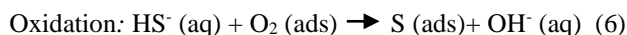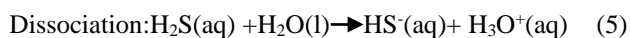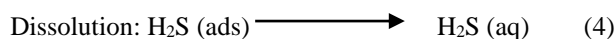
Adsorption Mechanism Of H_2S On Zeolites

Zeolite-based adsorbents have high H_2S breakthrough capacities hence they are possible alternatives for H_2S removal for instance ZnO-modified zeolites, CuO modified zeolites and ion-exchanged zeolites [13]. The basicity of these adsorbents initiates redox reactions resulting in effective H_2S removal. It was proposed that the following mechanism (equation 1 and 2) of the removal of H_2S using Zn and Cu impregnated/modified 13X zeolites occurs [15]. They suggested the possibility of the presence of copper and zinc as oxides in the impregnated zeolites. They proposed that H_2S adsorption is due to the basic oxides CuO or ZnO which react with H_2S as shown in Equations 1 and 2.

$$ZnO + H_2S \longrightarrow H_2O + ZnS \qquad (1)$$

$$CuO + H_2S \longrightarrow H_2O + CuS \qquad (2)$$
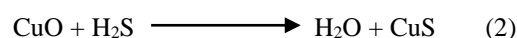
The mechanism of the removal of H_2S by Sigot et al., 2016a showed that it involves the adsorption of H_2S on the surface, dissociation of H_2S in water in the pores, and oxidation that

results in the formation of water and elemental sulphur [30]. They proposed the following steps, equation 3-6:

Adsorption: H_2S (g) ⟶ H_2S (ads)   (3)

Dissolution: H_2S (ads) ⟶ H_2S (aq)   (4)

Dissociation: $H_2S(aq) + H_2O(l) \rightarrow HS^-(aq) + H_3O^+(aq)$ (5)

Oxidation: HS^- (aq) + O_2 (ads) ⟶ S (ads) + OH^- (aq)   (6)

The adsorption step (Equation 3) underlines the importance of the characteristics of the adsorbent such as pore size and volume, and specific surface area. Then the dissolution step (Equation 4) shows the part played by water contained in the adsorbent pores implying that water amounts should be enough [31,32]. This step is also controlled by the morphology of the adsorbent since pores must be small enough to allow water film formation even at low humidity but big enough to contain the adsorbate and oxygen molecules [32].

A dissociation step (Equation 3) also shows the significance of water and the role of pH which is an important factor in the final speciation of sulphur [30,]. The role of oxygen is shown in equation 6, and it was reported that insufficient oxygen can hinder oxidation reactions before the pores could be filled with sulphur [30,33]. Sigot et al., 2016a found out that metals that might be present in the zeolite and the formed sulphur catalyse the oxidation of H_2S, entailing that the more sulphur that is formed, the more oxidation of H_2S [30]. This mechanism may be affected by other impurities particularly carbon dioxide and humidity present in the biogas.

2.1.1.2 Activated Carbon

In general, there are three types of activated carbon (AC) that are available and these are;

- catalytic impregnated which is regenerable,

- non-impregnated carbons (the virgin type) and

- impregnated carbons.

Different AC have been applied in the removal of H_2S to produce elemental sulphur and a little sulphur dioxide [34]. The impregnated AC are those carbons which have been mixed with a liquid or solid chemical before, during and/or after activation. The chemicals that are normally used in impregnation include sodium carbonate, potassium hydroxide, potassium permanganate, potassium iodide, sodium carbonate and sodium bicarbonate [35]. A typical caustic impregnated carbon has H_2S loading capacity of about 0.15g per gram of AC which is higher than the loading capacities of non-impregnated AC which are around 0.02 g per gram of AC. The advantage of ACs impregnated with a strong base is that they are regenerable by the use of a strong base, but the process is quite cumbersome on small scale processes, and in some instances the used adsorbent and area of treatment are classified as hazardous.

As for catalytic AC, the hydrogen sulphide loading capacities are about 0.10 g per gram of AC according to the ASTM D-6646 test method. The catalytic ACs are manufactured by treating AC with urea or chemicals that contain nitrogen such as ammonia which react with AC surface sites resulting in addition of nitrogen functionalities. The catalytic AC can be regenerated but large volumes of water are required.

It has been reported that for fuelling a fuel cell, rigorous H_2S removal by adsorption is required [30,36]. Sigot et al., 2016 (b) carried out a study where they compared the efficiency of different adsorbents (coconut-based AC, silica gel and 13X zeolite) on H_2S removal in a synthetic gas and they found out that the zeolite was the best with an adsorbed quantity higher than 75 mg of H_2S/g of zeolite [37]. Micoli et al., 2014 also studied the removal of H_2S using AC and zeolites, their study found out that H_2S removal was better with ACs than zeolites [15]. Sigot et al., 2016b did a comparative study on the removal of H_2S using three different commercial adsorbents (silica gel, activated carbon and zeolite) from a synthetic polluted gas on a lab-scale and they found out that the 13X zeolite performed the best [37].

Factors Affecting H_2S Removal By AC

Bashkova et al., 2007 reported that the surface properties, sizes of the pores and levels of nitrogen of AC have an effect on H_2S breakthrough capacity and elemental sulphur formation [38]. However, other researchers concluded that the chemistry of AC surface particularly acidity is a key factor in H_2S breakthrough capacity instead of surface areas and pore volumes [39]. Xiao et al., 2008 found out that the moisture content of the gas and alkali-impregnation play an important role on H_2S removal by AC [40]. When there is water in the biogas, the adsorption capacity is reduced due to water reacting with carbon dioxide forming carbonates that contribute to sulphurous acid formation which inactivates the catalytic sites.

It has been shown that pH plays an important role on the adsorption capacity and product distribution [41]. When the surface of AC has low pH, the S is highly oxidized to produce species that are water soluble and less elemental sulphur but there is an indirect proportionality between the total sorption capacity and acidity. It has been reported that the selection of non-impregnated AC for H_2S removal should rely mainly on the surface parameters that are related to its acidity [42,43]. At pH 5, significant adsorption capacities have been observed but high acidic conditions which decrease H_2S dissociation suppresses the process. When the number of acidic groups exceeds a threshold of about 0.85 mequiv/g of C, the capacity drops significantly.

Yan et al. 2004 reported that, when the pH is above 7, chemisorption of H_2S on hydroxyl (OH^-) sites on AC surface is favoured to form HS^- leading to a high ratio of HS^-/O^* promoting partial oxidation of sulphur species that results in the formation of different forms of solid sulphur [44]. They also discovered that, when the pH is between 4.5 and 7.0, there is a significant adsorption on a wet AC surface. The HS^-/O^* leads to the formation of sulphur oxide species that

make AC surface acidic, blocking pores as a result of the formation of sulphuric acid. Conversely, when the AC surface pH is below 4.5, the dominant process is physical adsorption and the formation of sulphuric acid increases. The formation of low pH surface reduces the rate of H_2S adsorption significantly resulting in reduced removal rate.
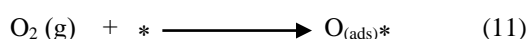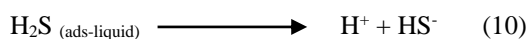
Bagreev and Bandosz., 2002 studied four different types of impregnated AC and they found out that as the concentration of sodium hydroxide used for impregnation was increased, breakthrough capacity of H_2S increased 4-5 times until a maximum of 10% sodium hydroxide was reached [45]. Bandoz., 2002 did a study where she used various ACs derived from different sources and found out that the H_2S adsorption efficiency depended on surface chemical properties and porosity [46]. They reported that an acidic surface improved H_2S conversion to sulphur dioxide and sulphuric acid but with small removal capacity whereas a basic environment promoted H_2S conversion to elemental sulphur with high removal efficiency.

Adsorption Mechanism of H_2S on AC

Bagreev et al. 2001(a) and Xiao et al. (2008) proposed a mechanism for H_2S oxidation/removal by AC and it involves the vapour, liquid, and solid phases [39,40]. The H_2S dissolves in the extremely thin film of water from the condensation of the vapour on AC and dissociates to hydrogen (H^+) and hydrogen sulphide (HS^-) ions. The dissociated HS^- and adsorbed oxygen on AC active sites are converted to elemental sulphur and water (net reaction shown in equation 7). On the other hand, some of the HS ions are oxidised forming sulphuric acid (net reaction shown in equation 8).
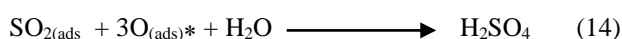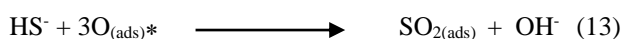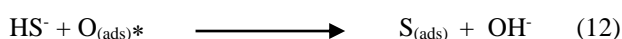
$$H_2S + \tfrac{1}{2}O_2 \longrightarrow S + H_2O \ (aq) \quad (7)$$

$$H_2S + 2O_2 \longrightarrow H_2SO_4 \quad (8)$$
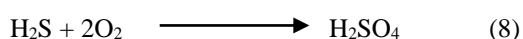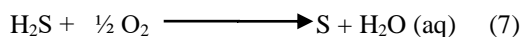
The proposed steps involved on the AC surface are shown in equations 9 to 15 [39,40].

$$H_2S\ (g) \longrightarrow H_2S\ _{(ads\text{-}liquid)} \quad (9)$$

$$H_2S\ _{(ads\text{-}liquid)} \longrightarrow H^+ + HS^- \quad (10)$$

$$O_2\ (g) + \ast \longrightarrow O_{(ads)}\ast \quad (11)$$

where: $\ast$ is active sites on activated carbon.

O_{ads} is the dissociative adsorbed oxygen.

$$HS^- + O_{(ads)}\ast \longrightarrow S_{(ads)} + OH^- \quad (12)$$

$$HS^- + 3O_{(ads)}\ast \longrightarrow SO_{2(ads)} + OH^- \quad (13)$$

$$SO_{2(ads)} + 3O_{(ads)}\ast + H_2O \longrightarrow H_2SO_4 \quad (14)$$

$$H^+ + OH^- \longrightarrow H_2O \quad (15)$$

The above proposed mechanism especially equations 9 and 10 show the importance of water on the surface of AC implying that both humidity and AC hydrophilicity greatly influence the removal of H_2S. There is a direct proportionality between the H_2S removal efficiency and relative humidity values and hydrophilicity [40]. It was also reported that H_2S dissociation and removal was improved when they modified AC by impregnation with sodium carbonate due to improved water adsorption [40].

Micoli et al., 2014 also modified activated carbons using bases resulting in higher performances than unmodified AC [15]. They proposed that the reason for the increase in performance is due to the increase in concentration of basic groups on treated ACs which leads to stronger interaction with H_2S. Due to the complex nature of the surface of ACs, the mechanism of adsorption of H_2S can be related to a lot of adsorbing sites such as dipole-dipole interactions that could occur between the H_2S and phenolic groups.

2.1.1.3 Iron Oxide Adsorbent

Iron sponge is a common and well-known iron oxide/hydroxide adsorbent. Abatzoglou & Boivin., 2009 reported that wood chips that are impregnated with iron can adsorb H_2S and mercaptans selectively. The hydrated oxides of iron of alpha and gamma structures are primary active ingredients although mixed oxide ($Fe_2O_3.FeO$) also contribute to adsorption. Crynes, 1978 proposed the following chemical reactions according to equations 16 and 17.

$$Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O \quad (16)$$

$$Fe_2S_3 + 3/2O_2 \rightarrow Fe_2O_3 + 3S \quad (17)$$
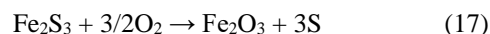
H_2S removal using iron sponge can be done in batch mode with separate regeneration, or with little air flow in the gas stream to allow regeneration. The regeneration is done under the following conditions: (i) gas stream oxygen concentration of 8%vol and (ii) a velocity of 0.3–0.6 m^3 per m^3 of the iron sponge per minute. Regeneration can also be done by removing the sponge and spread it out in a 0.15 m thick layer, and then wet it for ten days. The activity of the iron-sponge decreases by a third after every regeneration cycle thus it will need to be replaced at one point usually after the second use.

2.1.1.4 Adsorption Using Treated Sewage Sludge

The adsorption of H_2S by dry thermally treated sludge from municipal wastewater treatment is normally used to lower the concentration of H_2S prior to (i.e., pre-treatment) cleaning with another biogas upgrading technique such as AC. This will make AC capable of dealing with biogas with lower concentrations of H_2S and extending its operational life thus making the process cost effective. The ability of sludge to adsorb hydrogen sulphide has been investigated by a few researchers

The sewage sludge is an inexpensive starting material to obtain adsorbents. Gutiérrez Ortiz et al., 2014 investigated on the use of three kinds of sewage sludge that were thermally treated to remove H_2S from biogas in a fixed-bed column
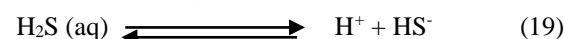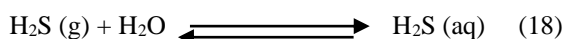
[47]. Their results showed that the adsorption capacities were almost the same and were also better than that of non-impregnated commercial AC but lower than sodium hydroxide impregnated commercial AC.

Bagreev and Bandosz., 2004 investigated the adsorption capacity of thermally treated sewage sludge [48]. The resulting adsorbents had surfaces which were alkaline after pyrolysis between 600-950 °C and had a breakthrough capacity of 0.115 g H_2S/g of adsorbent in an adsorption column with the following conditions (relative humidity (80%), H_2S concentration (3000ppmv), and gas flow rate of 0.5 L/min). On the other hand they used metal containing adsorbents derived from pryrolyzed sludge from industries and oils to study H_2S removal [49]. They proposed a mechanism that H_2S adsorption depended on porosity of the adsorbent, chemistry of the adsorbent surface and the moisture content and elemental sulphur was the major product. In a different study by Seredych et al., 2008, adsorbents were produced from a mixture of various compositions of sewage sludge and fly ashes (FA) by heating at 950 °C [50]. The FA was found to reduce H_2S removal capacity probably due to its hydrophobicity and it was dependent upon the content and type of FA as well as biogas composition.

2.2 Removal by Absorption

This process involves passing biogas through alkaline solutions such as sodium hydroxide and calcium oxide. These reactive absorption methods are not feasible methods because they are not selective as carbon dioxide also reacts with the alkaline solution consuming the expensive alkalis. Furthermore, the carbon dioxide is a valuable gas that can used for different applications. A schematic representation of the biogas upgrading process using chemical absorption is shown in Fig. 2.

H_2S removal using chemical absorption was studied by Horikawa et al., 2004 where they used iron-chelated solution catalysed by Fe/EDTA, where the H_2S is converted to elemental sulphur. Their results showed that high levels of H_2S can be eliminated in the catalytic solution when compared with water under the same conditions. In a continuous process, their results showed that it is a possibility to completely get rid of H_2S from biogas using prepared catalytic solution. H_2S chemical absorption process using iron-chelated solutions has advantages which include; low usage of chemicals since solutions work as a regenerable pseudo-catalyst, very good H_2S removal efficiency and selective removal of H_2S. The following mechanism (equation 18 - 20) was proposed for the iron chelating process in H_2S removal. The first step involves the absorption of H_2S into water (Equation 18) and dissociation occurs according to equations 19 and 20 [51].

$$H_2S \text{ (g)} + H_2O \rightleftharpoons H_2S \text{ (aq)} \qquad (18)$$

$$H_2S \text{ (aq)} \rightleftharpoons H^+ + HS^- \qquad (19)$$

$$HS^- \longrightarrow H^+ + S^{-2} \qquad (20)$$

The formation of elemental sulphur occurs through sulphide oxidation by the chelated iron as shown in equation 21.

$$S^{-2} + 2Fe^{+3} \longrightarrow S^0 + 2Fe^{+2} \qquad (21)$$
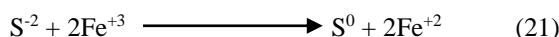
Regeneration occurs through conversion of the pseudo-catalyst into its active form Fe^{+3} according to equation 22 which occurs after oxygenation of the solution.

$$\tfrac{1}{2} O_2 + 2Fe^{+2} \longrightarrow 2Fe^{+3} + 2OH \qquad (22)$$
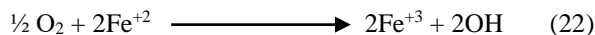
The elemental sulphur that is produced in the iron chelated based process can be easily recovered from the slurry through filtration or sedimentation processes under ambient temperatures which is an advantage [52].
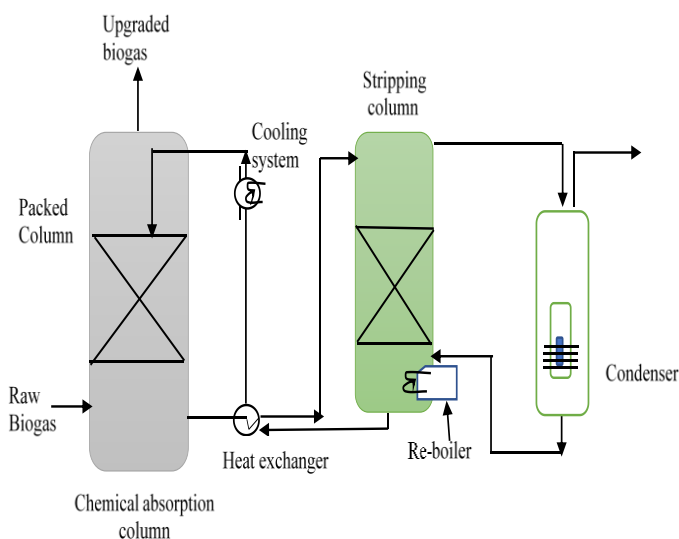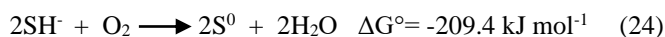

Fig. 2: Schematic representation of biogas upgrading process using chemical absorption [53].

2.3 Biological Removal of H_2S from Biogas

Biogas treatment by biological processes to remove H_2S have shown and has been reported to be a proper method because it has low operating costs, low chemical usage, and low energy costs than traditional physical and chemical processes. It is based on the use of sulphur oxidising microorganisms capable of oxidizing hydrogen sulphide in the presence of O_2 as an electron acceptor. Different stages were proposed for the biological oxidation process through several intermediates as shown in the equation 23 [54,55].

$$SH^- \longrightarrow S^0 \longrightarrow S_2O_3^{2-} \longrightarrow S_4O_6^{2-} \longrightarrow SO_4^{2-} \quad (23)$$
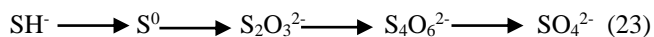
The microorganisms which bring about oxidation of sulphide relies on conditions and quantities of O_2 available although some microorganisms such as *Thiomicrospira sp.* and *Thiobacillus sp.* are able to perform the oxidation under anaerobic conditions [56]. Medigan et al., 2009 proposed the following reaction mechanism as shown in equation 24-26 [57]:

$$2SH^- + O_2 \longrightarrow 2S^0 + 2H_2O \quad \Delta G^\circ = -209.4 \text{ kJ mol}^{-1} \quad (24)$$

$$2S^0 + 4H_2O + 3O_2 \longrightarrow 2SO_4^{2-} + 2H^+ \quad \Delta G^\circ = -587.1 \text{ kJ mol}^{-1} \quad (25)$$

$$H_2S + 2O_2 \longrightarrow SO_4^{2-} + 2H^+ \quad \Delta G^\circ = -798.2 \text{ kJ mol}^{-1} \quad (26)$$

When there is limited oxygen, the main product will be elemental S whereas sulphate dominates when oxygen is readily accessible [58]].

### 2.3.1 Microbial Removal of Sulphur Compounds

The removal of sulphur compounds by microbial process is dependent on the biological cycle of sulphur. Oxidation and reduction reactions take place in the cycle. In the metabolic reactions used by a variety of microorganisms, sulphates are used as the electron accepting carriers (reduction process). For the oxidation process, sulphur compounds that will be reduced will function as electron donors that will aid the chemo lithotrophic or prototrophic bacteria. These bacteria help in the conversion of the sulphur compounds into sulphate or elemental sulphur. The disproportionation of sulphur is caused by highly specialized bacteria and some species that reduce sulphates. In such scenarios, the thiosulphate or elemental sulphur will function as both an electron acceptor and donor which will in turn result in simultaneous formation of sulphide and sulphate.

The Photosynthetic Van Niel Reaction has been reported by Barbusinski and Kalemba in 2016, to be a biotechnological process that can be used for H_2S removal [59]. The bacteria of the family *Chlorobiaceae* and *Chromatiaceae* can catalyse removal of H_2S under carbon dioxide with light to produce elemental S as shown in equation 27.

$$2nH_2S + nCO_2 \rightarrow 2nS^+ (CH_2O)n + nH_2O \quad (27)$$
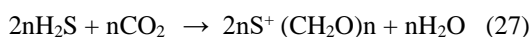
However, these photosynthetic bacteria pose some drawbacks because they are anaerobic in nature, and they also require radiant energy. The prototrophic bacteria also have a disadvantage of internally storing the produced sulphur, thus making it impossible to separate sulphur and cells.

Chemolithoautotrophic bacteria can as well be used in the removal of sulphide via the oxidation process of sulphide into sulphate or elemental sulphur. The genus *Thiobacillus* group has posed to be very effective in the removal of the sulphide as the bacteria has a stronger affinity for the sulphides and also works in aerobic conditions.

$$2HS^- + O_2 \rightarrow 2S + 2OH^- \quad (28)$$

$$2HS^- + 4O_2 \rightarrow 2SO_4^{2-} + 2H^+ \quad (29)$$
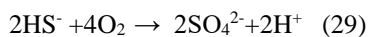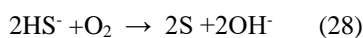
The most outstanding advantages of the biological removal of H_2S, is the ability to use ambient conditions, it is easy to operate and inexpensive. The biological removal of the sulphide also tends to be ecologically clean as most of the by-products are water, CO_2, sulphates, and nitrates.

In 2013, Ramos and friends devised a new microbial technology for H_2S removal [60]. They utilized the micro-aerobic desulphurization unit (MDU) as a new biological unit for H_2S removal. The reproduction of desulphurization conditions in the microaerobic digesters was done in the MDU external chamber. To be able to treat the produced biogas in the pilot chamber, a 1L of digested sludge was inoculated in a 10L unit. After over 100 days of research, the efficiency of the MDU was tested for H_2S removal and the efficiency of about 94% was achieved. The unit evidenced to be a robust process against alternations in biogas residence time ranging from 57mins to 107 mins, at an inlet concentration of H_2S of 0.17-0.39%v/v and temperature of 20-30°C. A minimum of three genera of sulphide-oxidizing bacteria were confirmed to be present after the microbiological analysis. They also had a recovery of 60% of oxidized H_2S in the form of solid elemental S in form of multi-layered sheets at the bellow the system with a purity of 98w/w.

2.3.2 Biofilters

These are fixed bed reactors that lack a mobile liquid chase used for the immobilization of microorganisms. It is made up of a porous material in which the contaminated gases flow through. The gases are then diffused into the biofilm (made of microflora) subsequently followed by biological oxidation.

The H_2S biofiltration mechanism has three major steps namely:

- The conversion of contaminated air containing H_2S from gaseous form to the aqueous form.

- Adsorption of contaminants by packing material and biofilm via diffusion.

    When the process of biodegradation occurs, the metabolic reaction and activities are carried out by the microorganisms on the bed material. The bed materials that have been used for the removal of H_2S include wood barks, pig manure and sawdust, cell-laden Ca-alginate, ceramics, porous silica packing and acid resistant polyethylene (AAB material).

The choice of the bed material is dependent on its effectiveness in removing high H_2S percentages in biogas, stability of the biofilter, uniformity of material, homogeneity, and the price of the material. Cheaper yet effective materials are preferred.

2.3.3 Biotrickling Filter Technology

This procedure involves the flow of gas through a fixed bed. An aqueous solution is incessantly added to the bed ensuring that the nutrients required by the biotrickling filter system are always readily available. The packing material must have a provision of necessary surface required for gas-liquid contact as well as biofilm attachment. The packing also contains microorganisms that grow as biofilm. Basically, the packed bed consists of an inactive material such as structured plastic packing, glass, lava rock, glass beads or rock wool.
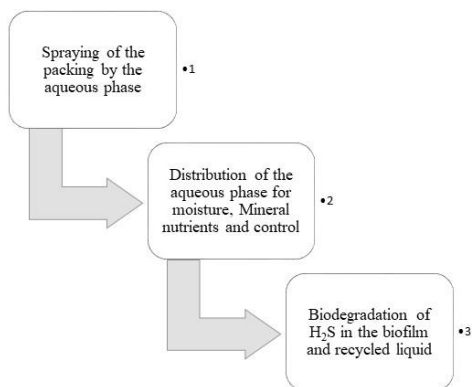
Fig. 3: Biotrickling process [60].

The biotrickling filter process is an efficient way of removing H_2S leaving elemental sulphur as the main product however, the S that is produced after desulfurization tends to be insoluble in water which in turn causes clogging of the packed bed. The use of porous material slightly reduces the clogging, but it is also necessary for the Biotrickling filter to be continuously washed to remove elemental S using back flushing for the stable operations of the bioreactors. Fig. 3 shows a general biotrickling process.

2.3.4 Biological Bubble Columns

Due to the drawbacks of clogging whilst using Biotrickling filters, biological bubble columns (BBCs) have been utilized as there can be the recycling of elemental sulphur without clogging. Whilst utilizing this column, firstly, there is the absorption of H_2S by an absorbent within the chemical absorption column followed by conversion of the absorbed H_2S to the elemental S, sulphite, or sulphate by microorganisms. San Valero and colleagues in 2019, reported that, coupling a BBC and an absorption column is efficient as over 81% of the 5000ppmv of hydrogen sulphide was eliminated from biogas with a ratio of elemental S in desulfurization exceeding 96% [61]. Though this process is efficient, it is an expensive method as it requires a larger space, and it also consumes a lot of chemical reagents.

2.3.5 Bioscrubbing

This process involves the use of a 3-phase fluidized-bed bioreactor that consists of an absorption tower and bioreactor. Pollutants in the biogas such as H_2S are absorbed in a recirculated liquid in a gas-liquid contactor. Regeneration of the pollutant laden liquid is done using microorganisms that will be in the liquid. The biochemical and physical processes are used for the removal of contaminated air. Initially, the malodourous components are absorbed in the aqueous phase, followed by physical adsorption of high molecular weight compounds by biological flocs.
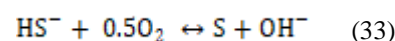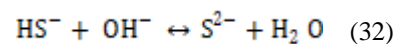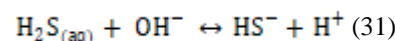
Tilahun et al (2018) and colleagues conducted the biological removal of H_2S using a novel hybrid polydimethylsiloxane (PDMS) membrane bio scrubber [61]. They inspected the optimum parameters required for H_2S removal. The effect of

the biogas flow rate, pH of the absorption liquid and DO concentration and the selectivity of H_2S were inspected. The best results in terms of H_2S selectivity and H_2S capacity removal came when using neutral pH compared to alkaline conditions. Upon increasing the gas flow rate by 32 l/d, the selectivity of desulfurization of H_2S/CO_2 and H_2S/CH_4 also increased. The methodology that was employed in this project had an efficiency of greater that 97%. It was also observed that the oxidation of H_2S was dependent on the amount of oxygen available. When oxygen is readily available, the H_2S is completely oxidized to elemental sulphur and if there is limited sulphur, it is converted to sulphate. The oxidation process occurs in the following process, equation 30-34.
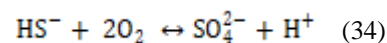
The malodorous gas is converted to aqueous phase.

$$H_2S_{(g)} \leftrightarrow H_2S_{(aq)} \qquad (30)$$
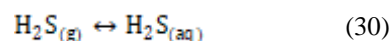
Oxidation process with readily available O_2

$$H_2S_{(aq)} + OH^- \leftrightarrow HS^- + H^+ \quad (31)$$

$$HS^- + OH^- \leftrightarrow S^{2-} + H_2O \quad (32)$$

$$HS^- + 0.5O_2 \leftrightarrow S + OH^- \quad (33)$$

Under limited oxygen conditions

$$HS^- + 2O_2 \leftrightarrow SO_4^{2-} + H^+ \quad (34)$$

The concentration of H_2S is lower than that of CO_2 in biogas but they however have analogous acidic behaviour and can both experience alkaline absorption hence for the efficient H_2S removal, the pH of the absorption liquid has to be highly basic. This leads to the operational cost being a bit expensive. Since CO_2 behaves in a similar way as H_2S, the removal of CO_2 as well is minimized by utilizing dense PDMS membranes because they have a higher selectivity towards H_2S.

3 Challenges

From the economical and operational point of view, adsorbent regeneration is compromised by the formation of stable sulphur polymers. This means that very high temperatures are required for the desorption process to occur. Sigot et al (2016)c explored the effects of other impurities in biogas on the removal H_2S [62]. They found out that the presence of moisture reduced the adsorption of H_2S on 13X zeolite resulting in reduced removal of the gas. The water was found to promote quicker saturation of the 13X zeolite adsorbent due to competition between the water and H_2S. On the other end contrary to this, they found out that removal efficiency of impregnated activated carbon (IAC) to remove H_2S was improved implying that humidity is necessary for effective removal of H_2S using IAC. The presence of impurities has different effects on the behaviour of different adsorbents due to the difference in the adsorbent hydrophilic or hydrophobic properties and textural properties. This shows that when the zeolite is used for H_2S removal from

biogas, there is a need for proper dehumidification for effective desulfurization.

Since biogas is a mixture of polar (H_2O/H_2S) and non-polar (methane) gases, a non-polar adsorbent cannot be used for the separation of H_2S. This means that a polar adsorbent surface is required for the separation of H_2S/CH_4 mixture. Alternatively, the presence of water whose dipole moment is higher than that of H_2S poses some challenges in the separation process. This means the use of amino-functionalised groups could be an alternative since H_2S is a stronger acid when compared to water, but there are limits associated with the use of amines as far as CO_2/H_2S separation is concerned because of the higher acidity of CO_2 with respect to H_2S [13]. Since both H_2S and carbon dioxide are Lewis acids, their separation by adsorption would not be effective because selective adsorption of H_2S will be difficult [63].

4. Conclusions and Recommendations

The review aimed to give an overview of different methods and the proposed mechanisms for H_2S removal for each upgrading technique. The manuscript highlighted the importance of the purification of biogas with special focus on H_2S removal hence it should be done irrespective of the end use of the biogas. The paper has reviewed literature on removal of H_2S using different techniques and the proposed mechanisms involved in its removal where possible. Methods which include physicochemical methods, adsorption, absorption, and biological processes among others have been explored. It has been noted that for adsorbents to be successful in H_2S removal, they should have a stable structure, good regenerability and sulphur loading capacity. The zeolites modified with metals or metal oxides have been shown to have high sulphur capacity hence they are promising materials for adsorption. The authors therefore recommend further research on the use of different adsorbents to come up with the most effective one taking into consideration lifespan and costs.

The use of commercial upgrading techniques such as water scrubbing, cryogenic separation and biological methods have a drawback of being costly both when investing and operating. These methods will make the end product more expensive such that poor communities who are really in need of the biogas may not afford. Therefore, the use of cheap natural adsorbents seem to be ideal but there is little information on their use hence more work needs to be done in this area. The major advantage of these materials is that they are readily available making the process easy.

Since a cost-effective method is always desired as far as the economical aspect is concerned, the authors recommend the optimization of any chosen method for H_2S removal. As several methods are available for H_2S removal, it is highly recommended that the levels of H_2S in the biogas to be cleaned be determined to help on deciding on which method to use for the best results. Since no single method will be able to remove all the contaminants present in the biogas effectively, more than one method can be used in series so

that the end product will be methane rich. The costs of the methods need to be calculated to see if it will be feasible and self-sustaining before investing into it. It is also desirable to develop a method that can remove H_2S and other impurities too present in the biogas as this will reduce the operational costs and makes the biogas affordable to poor communities.

There has been not much improvements in the study of the mechanisms involved in H_2S removal hence the authors recommend that more studies be conducted on understanding the mechanisms so as to help in the improvement of the effectiveness of the abatement techniques. This would greatly improve the quality of the resulting biogas and reduce greenhouse emissions. The understanding of the mechanisms involved will also help in designing materials with high regenerative capacity and easily reversible structures. Therefore, based on the mechanisms presented in this review, it can be concluded that, it is very possible to design and construct efficient biogas upgrading plants for the removal of H_2S and also to develop cost effective materials with a high H_2S removal efficiency although the presence of CO_2 might make it complicated. The successful design will then help to address the increasing energy demand and organic waste management thus improving the economic situations of the people in the communities.

Acknowledgements

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