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ANALYSIS AND EVALUATION OF THE BIOGAS PURIFICATION TECHNOLOGIES FROM $\rm H_2S$

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Abstract. H_2S concentrations in biogas are limited by environmental regulations. Because these gases are toxic to human health, cause corrosion, and damage the combined heat and power (CHP) engines and other metallic parts after burning. Hence, the following requirements must be met by a biogas purification method: 1 – high H_2S removal efficiency (RE), 2 – stability over a long period of time, 3 – low cost, 4 – minimal biogas dilution, and 5 – straightforward structure. There are various physical, chemical, and biological technologies, which can be undertaken to meet earlier mentioned criteria and efficiently remove H_2S from biogas. In this study, electrochemical oxidation, adsorption by zeolite, pressure swing adsorption, adsorption on activated carbon, adsorption on metal oxides, adsorption on nano-particles, metal sulfide precipitation, water scrubbing, membrane separation, organic solvents (amine), microaeration, and purification by sulfur-oxidizing bacteria (anoxic, aerobic, anaerobic), will be introduced, while their pros and cons are compared and discussed in detail.

Keywords: H₂S, biogas, purification methods, physical technologies, chemical technologies, biological technologies.

Introduction

Anaerobic digestion is a supportable stage and monetarily accessible innovation that can create crude biogas from squandered natural materials through complex biochemical cycles (Zhang et al., 2022; Das et al., 2022a). Many elements influence the interaction effect for producing high-quality biogas and among them, working circumstances (for example pH, temperature, or maintenance time), and the design of the anaerobic digester (Bahraminia et al., 2020; Das et al., 2022b; Franco-Morgado et al., 2018; Khan et al., 2021). This innovation shows incredible potential for the administration of natural squanders produced from agriculture, industry, and metropolitan activities (Zhang et al., 2022). It is gotten from domesticated animals' fertilizer, agriculture build-ups, biodegradable pieces of metropolitan waste, wastewater slime, modern parks, normal decay processes, wastewater treatment cycles, and food deposits are modest and plentiful wellsprings of natural matter for biogas creation by means of anaerobic digestion (Khalil et al., 2019; Nhut et al., 2020; Hou et al., 2018). As a green elective fuel to petroleum gas, exhaustive biogas purging is expected preceding its application. Biogas can be utilized to create heat and steam, electric power, vehicle fuel, gas-powered motors (which requires H₂S expulsion) or turbines (which requires a severe siloxane evacuation), or could be utilized for petroleum gas lattice infusion (Das et al., 2022a; Torres et al., 2020; Zhang et al., 2022). The aim of the study is to determine the most important technologies for biogas purification from H_2S , emphasize on each method's variables, and sorption capacity and to fairly evaluate and compare their benefits against drawbacks from concept to implementation; relying on obtained research analysis results by other recently published scientific articles, and distinguish most important characteristics of the selected purification methods (such as RE (removal efficiency), temperature, humidity, pH, etc.) in the end, come up with a brief conclusion and nominating the most suitable option for laboratory-scale research analysis of H_2S removal from biogas.

1. Physical adsorption (dry technologies)

Crude biogas, a final result of Anaerobic Digestion, primarily comprises around 20–45% carbon dioxide, 40–70% methane, and more modest measures of different gases including water vapor (H₂O), and Oxygen (O₂), nitrogen (N₂) and ammonia (NH₃ for the most part) (Figure 1). CH₄ is the main wanted constituent in crude biogas for its

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calorific worth (Das et al., 2022a). In the best scenario that biogas is expected to be utilized as a transportation fuel or infused into flammable gas networks, it is important to eliminate destructive gasses like H₂S (Torres et al., 2020). Excessive exposure to H₂S can result in a variety of symptoms, including nausea, eye irritation, mild conjunctivitis, and irritation of the respiratory (Prasertcharoensuk et al., 2022; Das et al., 2022a). Depending on the environmental conditions, H_2S is responsible for the deterioration of materials caused by biogenic corrosion, the poisoning of catalysts during steam reforming, and the foul odor caused by sulfur-oxidizing microorganisms (Ghimire et al., 2021; Haosagul et al., 2020; Juntranapaporn et al., 2019). In addition, during combustion, H₂S is oxidized into acidic sulfur dioxide (SO₂), which can be extremely corrosive to metal surfaces (Ghimire et al., 2021; Nhut et al., 2020).



Figure 1. Composition of raw biogas in percentage (approximate data)

Physically adsorbing dissolved sulfide to the surfaces of additional adsorbents lowers the concentration of dissolved sulfides, which is known as adsorption (Gao et al., 2022). Its simple system, low device requirements, simple operation, mild operating conditions, and absence of wastewater generation are drawing more and more attention (Ma et al., 2022). Adsorbent surface compositions, specific surface area, and porosity appear to dominate sulfide adsorption (Jiao et al., 2022). Adsorbent desulfurization capacity is enhanced by suitable humidity or high temperature (Zhang et al., 2022). Dry desulfurization has the advantages of low energy consumption, straightforward regeneration, and low desulfurize pulverization rates (Jiao et al., 2022). In the diagram below (Figure 2), all of the possible methods implemented to physical absorption of H₂S from the biogas has been demonstrated.

1.1. Electrochemical oxidation

As an alternative method for controlling sulfide in geothermal brines, sewage, and caustic solutions, electrochemical (anode oxidation) methods have recently been introduced (Su & Hong, 2020) Oxidation reduces the concentration of sulfide species by forming a wide range of intermediates and final products, including disulfide (Sn²⁻), polysulfide (S_2^{2-}) , sulfite (S_3^{2-}) , thiosulfate $(S_2O_3^{2-})$, and sulfate (SO_4^{2-}) . Sulfide species are electrochemically active (Su & Hong, 2020). An ion-exchange membrane typically divides an anode for oxidation and a cathode for reduction to transport the ions in a reactor (Aryal et al., 2022). There are two types of electrochemical sulfide oxidation reactions: direct oxidation and indirect oxidation (Zhang et al., 2022). During the direct oxidation process, sulfide is oxidized to elemental sulfur (SO), sulfate (SO_4^{2-}) , sulfite (SO_3^{2-}) , or thiosulfate $(S_2O_3^{2-})$, which is related to the anode material used in the experiment (Zhang et al., 2022). From a financial standpoint, the oxidation of sulfur to elemental sulfur is preferred because it requires the fewest number of electron transfers and, consequently, the least amount of energy (Zhang et al., 2022).

- $(HS)^{-} + (OH)^{-} \rightarrow S^{0} + H_{2}O + 2^{e};$ (1)
- $(\text{HS})^{-} + 4(\text{H}_2\text{O}) \rightarrow \text{SO}_4^{2-} + 9\text{H}^+ + 8^{e-}; \tag{2}$

$$2S + 6(OH)^{-} \rightarrow S_2O_3^{2-} + 3(H_2O) + 4^{e-};$$
(3)

 $S + 6(OH)^{-} \rightarrow SO_{3}^{2-} + 3H_{2}O + 4^{e-}.$ (4)

The addition of oxidants like O_2 , chlorine, Ag^{2+} , Ce^{4+} , and so on is known as indirect oxidation (Zhang et al., 2022). In contrast to direct oxidation, indirect sulfide oxidation is usually a non-selective process, and the oxidants that are produced can also extensively react with organic compounds that can be oxidized (Zhang et al., 2022). As a result, the process has a lower efficiency than direct sulfide oxidation (Zhang et al., 2022). The platinum anode is a type of organic matter-oxidizing electrode material that has been used for a long time due to its stability and high electrical conductivity (Zhang et al., 2022). Platinum electrodes can selectively convert pollutants at low current density due to their relatively low oxygen evolution over potential (Zhang et al., 2022). Stainless steel is a cheap material that primarily consists of Fe, Ni, Mn, and Cr. An extremely effective anode for oxygen evolution in alkaline media can be made of stainless steel that has had its surface oxidation modified (Zhang et al., 2022).



Figure 2. Dry technologies to H₂S removal from biogas

1.2. Adsorption by zeolites

Zeolites are frequently used as catalytic materials because of their strong affinity and selectivity for polar compounds like H_2S (Kulawong et al., 2022). Zeolites are microporous crystals with three-dimensional SiO₄ and AlO₄ tetrahedra structures (Kulawong et al., 2022; Bahraminia et al., 2020). Among the variously studied zeolites, NaX zeolite and its ion-exchanged forms have been extensively utilized for H_2S removal (Kulawong et al., 2022; Zhang et al., 2022). To remove sulfur compounds in gas pipelines, it has been demonstrated that silver (Ag) exchanged zeolites are effective adsorbents with a high capacity and absorptivity (Kulawong et al., 2022). Zeolites are good adsorbents for gas separation applications because of their large surface area, uniform pore diameter, and large number of cationic active sites (Bahraminia et al., 2020).

1.3. Pressure swing adsorption

The selective adsorption of Hydrogen sulfide molecules over solid adsorbent surfaces as a result of surface chemistry or molecular sieve action underpins the PSA-based upgrading process (Abd & Othman, 2022). The adsorption mechanism is determined by the adsorbent's interaction affinity with H_2S molecules and the characteristics of its surface (Abd & Othman, 2022). The PSA operating conditions, such as the adsorption pressure, purge ratio, and desorption pressure, played an important role in the PSA's overall performance (Abd & Othman, 2022).

1.4. Adsorption by activated carbon

Activated carbon (AC) is a highly carbonaceous material with well-developed microporous structure and high specific surface area, which lead to an excellent adsorption capacity (Wang et al., 2022). It also shows great application prospects due to its low cost, high specific surface area, good adsorption capacity, excellent thermal and chemical stabilities, simple operation, and reusability. Adsorb H₂S up to a concentration of 1000 ppm at room temperature (Wang et al., 2022; Xu et al., 2022; Moradi et al., 2020). To enhance the adsorption of polar molecules, the nature of the activated carbon can be altered through surface modification without altering its porosity. Petroleum coke, wood, and coal are the main resources used to make AC (Wang et al., 2022). On the other hand, because they are neither renewable nor inexpensive, their widespread use of AC is somewhat constrained (Wang et al., 2022). Because of their developed pore structures, extensive application experience, and accumulation of engineering data in the fields of gas purification and separation, activated carbons have emerged as the most widely used adsorbents for the removal of gaseous H₂S (Ma et al., 2022). However, the limited availability of activated carbon's raw materials limits its widespread use and raises application costs (Ma et al., 2022).

1.5. Adsorption by metal oxides

Despite having developed pore structures and large specific surface areas, these porous materials' sulfur capacities remain extremely low during desulfurization (Jiao et al., 2022). As a result, they have been modified by supporting CuO, ZnO, Fe_2O_3 , and CaO (Jiao et al., 2022). CuO-modified materials presented better behavior even at smaller loadings (Jiao et al., 2022). Impregnation of metal compounds on carbon materials can boost the co-removal performance of H₂S. For this reason, the surface chemical properties of carbons can be modified with metal (Xu et al., 2022). However, MgO provides a mild and stable alkaline environment for the adsorption and catalytic oxidation of acidic gas H₂S in comparison to CuO and ZnO because of its higher alkalinity (Xu et al., 2022).

1.6. Adsorption by nano-particles

Choi et al. first proposed the new idea of nanofluids in 1995. Nanofluids are a promising new type of material that has been used in machining, solar energy systems, electronic equipment cooling, and heat exchangers (Ma & Zou, 2018). It is demonstrated that the mass transfer process can be enhanced by including fine particles in the adsorbent (Ma & Zou, 2018). Dagaonkar discovered that water, hexadecane, and sunflower oil's physical absorption of pure CO₂ could be enhanced by micron-sized TiO₂ particles (Ma & Zou, 2018). Kim used NH₃/H₂O solution at a concentration of 8% as the base fluid (Ma & Zou, 2018). The addition of nano-sized Cu, CuO, and Al₂O₃ particles could significantly enhance the NH₃/H₂O solution's absorption performance; this enhancement could be even greater at higher concentrations (Ma & Zou, 2018).

2. Chemical absorption (wet technologies)

Due to its simple operation, high efficiency, and adaptability, the chemical method of removing H₂S for industrial use looks promising. In the chemical method, alkanolamine, alkali, and an oxidant are frequently used to absorb H₂S (Gao et al., 2022). Ionic liquids and other absorbents are expensive; Consequently, it is challenging to implement them in the industry (Gao et al., 2022). As a result, it is critical to investigate a novel H₂S absorption method with high H₂S removal efficiency, low cost, and friendly to the environment (Gao et al., 2022). On the other hand, the mass transfer resistance at the gas-liquid interface makes it difficult to strengthen the reaction process when using wet processes to get rid of hydrogen sulfide (Ma & Zou, 2018). A diagram of possible chemical absorption technologies for H₂S removal from biogas is illustrated (Figure 3).



Figure 3. Wet technologies to H₂S removal from biogas

2.1. Metal sulfide precipitation

The addition of oxidants like ferric chloride, hydrogen peroxide, and hypochlorite to the substrate to convert the sulfide in the substrate into elemental sulfur, thiosulfate, or sulfate is known as "in situ" chemical oxidation (Zhang et al., 2022). Ferric salts, ferric oxide, ferric hydroxide, and hypochlorite are examples of reagents in both the liquid and solid phases (Zhang et al., 2022). Hypochlorite can oxidize sulfur to SO, but it tends to react with organic substrates, slows the activity of methanogens, and reduces biogas yield (Zhang et al., 2022). Hypochlorite, Cl₂, and KMnO₄ are all potent oxidants that have the potential to corrode equipment and pipelines, necessitating more money spent on equipment maintenance (Zhang et al., 2022). The catalytic activity and selectivity toward sulfur (S) have been reported to increase upon impregnation of transition metal salts, such as iron (Fe), copper (Cu), and zinc (Zn), in AC for increased capacities for H₂S adsorption (Choudhury & Lansing, 2021). Iron (III) salts like ferric hydroxides (Fe(OH)₃) and ferric chloride (FeCl₃) can also be added to get rid of H₂S (Zhang et al., 2022; Ghimire et al., 2021).

$$2Fe(OH)_3 + 3H_2S \rightarrow Fe_2S_3 + 6(H_2O);$$
 (5)

$$2\text{FeCl}_3 + \text{H}_2\text{S} \Rightarrow \text{S} + 2\text{FeCl}_2 + 2(\text{HCl}).$$
(6)

This technology isn't as good at getting H_2S levels low enough to meet the quality requirements for vehicle fuel or gas injection into a grid that is stable (Ghimire et al., 2021). Ferric chloride is also a coagulant that contributes to the thickening and separation of sludge (Zhang et al., 2022). Because it also has the potential to clog pipes and cause medium acidification, a higher dosage did not directly improve sulfide removal (Zhang et al., 2022).

2.2. Water scrubbing

The main principle is that CO_2 and H_2S are more soluble in water compared with CH_4 (Cuimei et al., 2018). The assertion of their attractiveness is contested by two challenging areas (Cuimei et al., 2018; Alkhatib et al., 2021). Scaling up the reported success of these solvents from lab-scale conditions to industrial-scale conditions is the first obstacle; simply because many necessary properties are currently unavailable. Extending experimental measurements for the wide range of thermos-physical and transport properties required for accurate and representative performance assessment at the industrial scale is impossible due to the taxing nature of experimental efforts (Alkhatib et al., 2021). The second obstacle is that, whenever experiments are carried out on a large scale in the laboratory, only a small number of criteria, particularly a high absorption capacity and a low enthalpy of absorption, are used to demonstrate a solvent's potential (Alkhatib et al., 2021). For the first challenge, scaling data from the laboratory to industry operating conditions can be resolved through the application of molecular modeling techniques and recent advancements in thermodynamic modeling approaches and computational capabilities (Alkhatib et al., 2021). For the second challenge, the demonstration of the potentiality of a selected solvent, which is typically attested with a limited number of criteria, the solution might appear to be rather intuitive, and it is the addition of additional (Alkhatib et al., 2021). Still, commercially available scrubbing systems for reducing high H₂S concentrations may have high capital and operating costs, unpredictability in terms of efficiency, and require proper management for effective operation (Choudhury & Lansing, 2021; Haosagul et al., 2020).

2.3. Membrane separation

The transfer of gas pollutants from one side of the membrane to the other in membrane bioreactors (MBRs) occurs when a biofilm forms on the membrane's surface and comes into contact with a mineral medium rich in nutrients (Santos-Clotas et al., 2020). Because of its consistent performance throughout the duration, it may be a suitable technology for the treatment of odors and the purification of biogas with high concentrations of H₂S (Das et al., 2022b). The main advantage of MBRs for waste gas treatment over conventional biotechnologies (i.e., biofilter) is the presence of a discrete water phase that allows optimal humidification of the biomass while preventing its inactivation (Das et al., 2022b; Santos-Clotas et al., 2020). The disadvantages of MBR include high investment costs (Santos-Clotas et al., 2020; Ma et al., 2022), poor membrane material stability (Ma et al., 2022), low adsorption capacity (Kulawong et al., 2022), and clogging and fouling as a result of excessive biomass growth (Santos-Clotas et al., 2020). When compared to other reactor configurations, membranes are capable of selectively permeating pollutants (Santos-Clotas et al., 2020).

2.4. Organic solvents (amine)

Due to its high acid gas affinity and absorption capacity specifically utilized for H_2S capture, the chemical absorption process employing aqueous solutions of organic amines, such as monoethanolamide (MEA), is the industry

standard (Irani et al., 2018; Alkhatib et al., 2021). It has been demonstrated that it enables raw biochar to possess larger specific surface areas and more rich surfaces functional groups, thereby enhancing the desulfurization effect (Ma et al., 2022). Alkanoamine-based solvents, also known as aqueous organic amines, are currently utilized extensively for the process of separating acid gases, such as hydrogen sulfide, from natural and industrial-based gases (Irani et al., 2018; Shi et al., 2022). In this process, the acidic components of the gas/liquid contactor undergo an exothermic-reversible reaction with the alkanoamine (Irani et al., 2018). On the other hand, using amine-based solutions for the absorption process has a number of drawbacks, such as the high amount of energy required to regenerate the solvent, its toxicity, equipment corrosion, and the loss of the solvent. Ionic liquids (ILs) have been widely used as absorbents for gases capture due to their outstanding advantages, such as almost no vapor pressure, high chemical stability, and excellent affinity with acid gases, in order to address the issue of energy consumption (Shi et al., 2022).

3. Biological filtration

The third method to H₂S removal from biogas is biological filtration. The biological methods are based on the implementation of oxidizing bacteria that live in places where there are sufficient sources of sulfur compounds like H₂S. (Pudi et al., 2022; Vikrant et al., 2018). Sulfur-oxidizing bacteria (SOB) are essential to the biological process's success (Pudi et al., 2022). Depending on the species, genus, and functional genes of the SOB, as well as the amount of oxygen present in the system, SOBs can convert sulfur compounds like hydrogen sulfide, sulfur, and thiosulfate to elemental sulfur or sulfate. These gram-negative bacteria have been divided into three domains-anaerobic, anoxic, and aerobic (Nhut et al., 2020; Haosagul et al., 2020). Generated sulfur compounds can be stored both inner and outer parts, and each one has different properties in the cells (Pudi et al., 2022). All domains share the following sulfur oxidation reactions (Pudi et al., 2022):

$$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4 + 2H^+ + SO_4;$$
 (7)

$$\mathrm{CO}_2 + 2\mathrm{H}_2\mathrm{S} \rightarrow \mathrm{CH}_2\mathrm{O} + \mathrm{H}_2\mathrm{O} + 2\mathrm{S}. \tag{8}$$

Below (Figure 4) a diagram of possible biological H_2S removal methods has been demonstrated.

3.1. Anaerobic bacteria

Photons are taken in by anaerobic oxidizing bacteria to provide energy for cell metabolism and growth (Pudi et al., 2022). In the photosynthetic reaction, CO_2 has a function like an electron acceptor and a carbon source, on the contrary, H_2S is the electron giver. Anaerobic light-dependent sulfide oxidation involves the following reactions (Pudi et al., 2022; Nhut et al., 2020):

$$2(H_2S) + CO_2 \rightarrow \text{presence of light} \rightarrow 2S^0 + CH_2O + H_2O;$$
 (9)

$$2(H_2S) + 2(CO_2) + 2(H_2O) \Rightarrow \text{ presence of light} \Rightarrow$$

$$SO_4^{2-} + 2H^+ + 2(CH_2O). \tag{10}$$

Light serves as an energy source for the phototrophic SOB's activity (Nhut et al., 2020). The concentration of sulfide affects the intensity of the light that SOB receives; The H_2S is oxidized into elemental sulfur at high light intensities (Nhut et al., 2020). Utilizing the digestate from the anaerobic digester as a water and nutrient source to support microbial growth has recently improved anaerobic bacteria devoted to biogas upgrading (Franco-Morgado et al., 2018). On the other hand, the characteristics of phototrophic bacteria are quite straightforward and they are simple to grow; however, their effectiveness is low, their growth rate is slow, the light source needs to be sufliciently strong, and the costs are high (Nhut et al., 2020; Franco-Morgado et al., 2018).

3.2. Aerobic bacteria

 O_2 is used as an electron acceptor by aerobic oxidizing bacteria (Das et al., 2022a; Haosagul et al., 2020). These bacteria use CO_2 as a carbon source and grow on H_2S as a source of energy (Pudi et al., 2022; Das et al., 2022a; Nhut et al., 2020; Jia et al., 2022; Ghimire et al., 2021; Vikrant et al., 2018). If oxygen is scarce in the system, the oxidation process will result in sulfur (H_2S/O_2) (Pudi et al., 2022; Ghimire et al., 2021). In addition, sulfur is transformed into sulfate (Nhut et al., 2020; Ghimire et al., 2021), if oxygen is continuously supplied.

$$H_2S + H_2O \rightarrow HS^- + H_3O^+;$$
 (11)

$$2(HS^{-}) + O_2 \rightarrow S^0 + H_2O;$$
 (12)

$$S^0 + H_2O + 0.5O_2 \rightarrow SO_4^{2-} + 2H^+.$$
 (13)



Figure 4. Biological technologies to H_2S removal from biogas (dark green) and the methods to implement them (light green)

Utilizing oxygen as an electron acceptor to oxidize H_2S is a normal procedure that these SOBs are involved (Pudi et al., 2022). This type of bacteria is outstanding beyond anaerobic SOBs because they can grow at high rates without light. Utilizing co-current flow in the absorption column, decreasing the recirculation liquid/biogas ratio (L/G), or dosing the digested directly into the absorption column are just a few of the strategies that have been tried and failed to lower the O_2 content of the upgraded biogas in order to adhere to the stringent O_2 levels set by biomethane standards (Franco-Morgado et al., 2018).

3.3. Anoxic bacteria

Nitrate (NO₃) serves as an electron acceptor for anoxic oxidizing bacteria (Das et al., 2022a; Haosagul et al., 2020). This type of desulfurization involves two steps. First, the nitrate-reducing sulfide-oxidizing bacteria (NR-SOB) convert H₂S into elemental sulfur, which is then transformed into sulfate (Juntranapaporn et al., 2019). The N/S molar ratio, which is the relationship between nitrate, which is represented as nitrogen, and H₂S, which is represented as sulfur, is the key to controlling the final oxidation product, preventing SO clogging, and maintaining a suitable pH for successful operation. As a result, a high sulfate production rather than elemental sulfur is typically desired (Juntranapaporn et al., 2019). H₂S is oxidized to sulfates without forming elemental sulfur in the presence of a low concentration of sulfide (Nhut et al., 2020).

$$5(H_2S) + 2(NO_3) \rightarrow 5S + N_2 + 4(H_2O) +$$

2(OH); (14)

$$5(H_2S) + 8(NO_3) \rightarrow 5(SO_4^{2-}) + 4N_2 + 4(H_2O) + 2H.$$
 (15)

Anoxic desulfurization can be performed using commercial nitrate, nitrate produced in a nitrification bioreactor, wastewater, or biogas digestion slurry to avoid the additional costs of procuring commercially available NO₃. However, a higher N/S ratio can decrease the pH of the packing bed phase, which may affect the reduction of nitrate to N₂ (Ghimire et al., 2021; Watsuntorn et al., 2020; Santos-Clotas et al., 2020).

Anoxic and aerobic SOBs are suitable for biodesulfurization because they meet the requirements of high sulfide loading rates, high H₂S removal efficiency, high adaptability to grow in a variety of conditions, and a simple source of nutrition (Nhut et al., 2020). Anoxic biological air filters overcome the disadvantages of aerobic systems, such as safety issues brought on by the formation of potentially explosive CH_4/O_2 mixtures, biogas dilution, and limitations on the mass transfer of nitrogen and oxygen (Ghimire et al., 2021; Juntranapaporn et al., 2019). It's important to note that anoxic desulfurization may be more selective for sulfate than aerobic desulfurization due to the difficulty of achieving high dissolved oxygen levels in the liquid phase when treating a high H₂S inlet load (IL) (Juntranapaporn et al., 2019). Biofilters (BFs) for biogas biodesulfurization have proven to be an effective method to remove H_2S at pilot and full-scale under aerobic conditions (Juntranapaporn et al., 2019). Despite these benefits, anoxic desulfurization is associated with higher operational costs due to the nature of the electron acceptor source (commercial nitrate). However, only pilot and laboratory-scale studies have been conducted under anoxic conditions (Santos-Clotas et al., 2020).

3.4. Biological filtration methods (bioscrubber, biotrickling filter and biofilter)

A common biological method for removing H₂S from the gas stream is bio-scrubbing. One of its main components is an absorption/separator chamber (Pudi et al., 2022). The first is a biological process, while the second is a physical one (Pudi et al., 2022; Das et al., 2022b). Preventing the escape of untreated air is essential by uniformly wetting the bed (Konkol et al., 2022). Large gas streams with high concentrations of pollutants (>0.5 g/m³), such as hydrogen sulfide, ammonia, or other sulfur compounds, can be effectively treated with these units (Konkol et al., 2022). The primary application for bio-scrubbers (BSs) is the removal of water-soluble single pollutants like H₂S, NH₃, or fatty acids (Das et al., 2022b). By altering the reactor design, BSs can also be utilized for the removal of mixed pollutants, such as two-liquid phases, spray columns, or two-stage systems (which consist of two bioreactor units: an airlift loop reactor unit and a liquid-impelled loop reactor unit) (Das et al., 2022b). A bio-scrubber also has some benefits, like being able to control nutrients and pH with ease, not adding oxygen or nitrogen to the sweet gas, working with water-soluble compounds like H₂S and high inlet loading rates, and being able to operate in a variety of conditions (like pH, temperature, or nutrients) (Pudi et al., 2022; Das et al., 2022b). The complexity of the operation and maintenance are two disadvantages of utilizing this technology (Das et al., 2022b).

Most of the time, the SOBs are moves through the media that they placed in, and produce a place that is structured by recirculating aqueous solution in a co-current or counter-current arrangement made by trickling solution (Pudi et al., 2022; Nhut et al., 2020; Juntranapaporn et al., 2019; Konkol et al., 2022). This arrangement enables the delivery of nutrients to the biofilm and the additional absorption of contaminants in the aqueous phase (Konkol et al., 2022). It can handle high H₂S concentrations at higher flow rates because the system's recirculating liquid can control pH, nutrients, and sulfate concentration to increase removal efficiency (Juntranapaporn et al., 2019). In a BTF, the loading rate is an obstacle factor that is affected by the rate of solution trickling and the solubility of contaminants in the biofilm's water layer (Pudi et al., 2022). The bed might not be sufficiently wetted at a very low trickling rate, which could slow down the H₂S transfer (Pudi et al., 2022). A high trickling rate can influence the formation of a liquid with high density, which restricts receiving of oxygen into the biofilm and consequently, reduces H₂S removal efficiency (Pudi et al., 2022). Pollutants must meet

certain requirements, such as molecular weight, chemical structure, and solubility, in order for the BTF system to function optimally (Nhut et al., 2020). In BTF, the most suitable compounds are those with low molecular weight and are highly soluble (Nhut et al., 2020). The device also needs a long time to get used to (Konkol et al., 2022).

In the end, a bio-filtration reactor typically consists of a column filled with biological materials like biochar, pine bark, peat, compost, and wood chip (Konkol et al., 2022). These materials are supplemented with nutrients by bacteria, and a diverse microbial community forms a biofilm in the process (Konkol et al., 2022). Even at low concentrations of contaminants (less than 1 g/m^3), bio-filters are ideal for removing odorous gases (Konkol et al., 2022). They cause the pollutant to biodegrade and be transformed into water and carbon dioxide, which are benign substances. At the industrial scale, these methods were found to achieve high H₂S RE with H₂S concentrations as high as 20.000 ppm (Nhut et al., 2020).

Conclusions

There are various methods and technologies introduced throughout this study, and each one's benefits and back draws indicated which should be taken into account in the selection process of intended H₂S purification from Biogas strategy. As stated before, these properties can have different impacts on the research outcome, hence must be chosen based on the main characteristics of the experiment like assumed budget, available material, technology, location (in-situ or laboratory), weather, humidity, temperature, and dedicated time.

Considering the nature of this study which concentrates on the development of environmental protection technologies, and waste management plays a crucial role in this matter, choosing Biological filtration of H₂S from biogas methods and technologies, is the most suitable option. Besides the fact they are consuming both waste and organic materials as packing medium (inside the bio-scrubber, bio-trickling filter, biofilter) will assist in end-up product management goals, also the function of these technologies is relying on natural interactions of living microorganisms which are not depending on adding other chemical substances that may have a negative impact on surrounding ecosystem (like the case of chemical technologies) or consume higher energy, and having enormous capital and maintenance costs (like in the case of physical technologies).

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$\rm H_2S$ VALYMO IŠ BIODUJŲ TECHNOLOGIJŲ ANALIZĖ IR VERTINIMAS

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Santrauka

 $\rm H_2S$ koncentracijas biodujose reglamentuoja aplinkosaugos teisės aktai. Šios dujos yra nuodingos žmonių sveikatai, sukelia koroziją bei pažeidžia šilumos ir elektros (ŠEV) variklius bei kitus mechanizmus. Taigi, taikant biodujų valymo metodą, turi būti tenkinami šie reikalavimai: 1 – aukštas $\rm H_2S$ šalinimo efektyvumas (ŠE), 2 – stabilumas ilgą laiką, 3 – maža kaina, 4 – minimalus biodujų skiedimas ir 5 – paprasta struktūra. Yra įvairių fizinių, cheminių ir biologinių technologijų, kurias galima naudoti, kad atitiktų anksčiau minėtus kriterijus ir būtų efektyviai pašalintas $\rm H_2S$ iš biodujų. Šiame tyrime aprašoma elektrocheminė oksidacija, adsorbcija naudojant ceolitą, slėgio svyravimo adsorbcija, adsorbcija su aktyvuota anglimi, adsorbcija ant metalų oksidų, adsorbcija ant nanodalelių, metalo sulfido nusodinimas, vandens šveitimas, membranų atskyrimas, organiniai tirpikliai (aminai ir mikrobai). Tyrimo metu bus pristatytas gryninimas sierą oksiduojančiomis bakterijomis (anoksinėmis, aerobinėmis, anaerobinėmis), o jų privalumai ir trūkumai bus lyginami tarpusavyje ir išsamiai analizuojami.

Reikšminiai žodžiai: H₂S, biodujos, valymo metodai, fizinė technologija, cheminė technologija, biologinė technologija.