

Reactive Processes for H₂S Removal

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Abstract: Growing demand for renewables and sustainable energy production contributes to a growing interest in producing high quality biomethane from biogas. Despite having methane (CH₄) as its main component, biogas may also present other noncombustible substances in its composition, i.e., carbon dioxide (CO₂), nitrogen (N₂) and hydrogen sulfide (H₂S). Contaminant gases, such as CO₂ and H₂S, are impurities known for being the main causes for the decrease of biogas calorific value and corrosion, wear of pipes, and engines, among others. Thus, it is necessary to remove these compounds from the biogas before it can be used in applications such as electricity production, thermal purposes, and replacement of conventional fossil fuels in vehicles, as well as injection into natural gas distribution networks. In this context, the present work aimed to present a systematic review of the literature using the multicriteria Methodi Ordinatio methodology and to describe processes and materials for H₂S removal. The discussion indicated new materials used, as well as the advantages and disadvantages observed and the limitations in industrial implementation.

Keywords: biogas purification; catalyst; H₂S removal



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1. Introduction

Some of the greatest challenges faced by urban cities are ongoing urbanization and socioeconomic development, the energy crisis caused by the depletion of fossil fuels and the billions of tons of organic waste generated by the municipal, industrial and agricultural sectors [1].

Food waste is the main component of municipal solid waste, with approximately 1.3 billion tons being generated globally each year [2].

The generation of renewable energy challenges companies become involved in a chain process where all links are co-responsible for the generation of new products, processes, and responsible consumption and production, with the goal of protecting the environment and improving people's quality of life [3].

Generally, organic waste management occurs through landfills, composting and incineration, but these processes are associated with high land and energy costs as well as greenhouse gas emissions; they also cause significant pollution [4]. Thus, more sustainable alternatives such as anaerobic digestion make it possible to recover energy-rich biogas, reduce residual production and generate nutrient-rich biofertilizers [5].

Anaerobic digestion is one of the promising waste-to-energy technologies that converts organic waste into useful gaseous fuel (biogas). In this process, methane is produced in the presence of methanogens (bacteria). The survival and activities of methanogens are based on several parameters, such as pH, temperature, organic load rate and types of biodigesters. Furthermore, these parameters influence biogas production in terms of yield and composition [3].

As for the conversion of food waste in a biorefinery on a commercial scale, according to Morone and Imbert (2020), some factors need to be considered, namely: the volume

and quality of food waste; information for the collection of food waste (improving the homogeneity of biobased products produced from food waste); the sources of food waste; transfer and storage; implementation of biobased policies; and increasing public awareness to improve the demand and supply of biological products [6].

Waste conversion is critical to sustainability; it can avoid adverse effects on biodiversity, avoid harming the soil and support the food industry. The profitable exploitation of waste is a complex and multidisciplinary problem as it requires knowledge of materials, technologies and market and socioeconomic issues related to the valuation of the secondary flow [7].

Despite the potential of biogas as a fuel, using it without adequate removal of H₂S has serious environmental implications resulting from the formation of SO₂ [8]. Thus, the removal of H₂S is essential to improve the quality of biogas and avoid the formation of corrosive species in combustion systems [9]. The main composition of biogas is indicated in Table 1.

Table 1. Biogas composition [10].

CH ₄	60–70%
CO ₂	30–40%
N ₂	<1%
H ₂ S	10–2000 ppm

Motivation

Biogas is a gaseous fuel that can be used for direct burning for various purposes. However, many uses of biogas require a purification process, such as the removal of sulfur (hydrogen sulfide–H₂S), ammonia (NH₃), carbon dioxide (CO₂) and other external elements. Dobsław et al. (2019), for example, indicated the use of biogas fuels in internal combustion (IC) engines. However, harmful emissions of NO_x, CO, particulate matter, NH₃, SO₂, H₂S and odor, as well as unburned volatile organic compounds (VOC) and polyaromatic hydrocarbons (PAH), may occur. Thus, an alternative low-cost waste gas treatment system was installed that used chemical scrubber with an optional subsequent biofilter for oxidative catalysts [11].

Selective removal of H₂S is even more essential when the biogas is used in turbines, cogeneration engines or as vehicle fuel. Different physical, chemical or biological routes can be used for this purpose. Some possible routes include physical adsorption [12] or absorption [13] processes that allow the transfer of the contaminant from one phase to another; chemical processes such as H₂S selective catalytic oxidation [14] or chemical scrubbing to form S⁰; and biodegradation processes, e.g., biotrickling filters (BTF) [15–17], which allow H₂S conversion into elemental sulfur or sulfuric acid, depending on the O₂ content. Figure 1 indicates some common types of processes used for this purpose.

That been said, reactive purification processes, such as those that convert H₂S into S⁰, stand out as they allow the transformation of the contaminant into a solid product that is easier and safer to separate and discard [8]. Biotechnological processes, such as BTF and bioscrubbers, are widely used for this purpose, but they require high levels of care that include cultivation and maintenance of micro-organisms, temperature and pH control, with abatement limitations for high sulfur contents [18,19]. Chemical or adsorption processes are not limited in this way but can involve significant costs related to the consumption of reagents and the replacement of adsorbents/catalysts [18,19]. Thus, processes that allow the regeneration of adsorbents [20] and catalysts [21] are preferable, as they allow reuse and costs reduction.

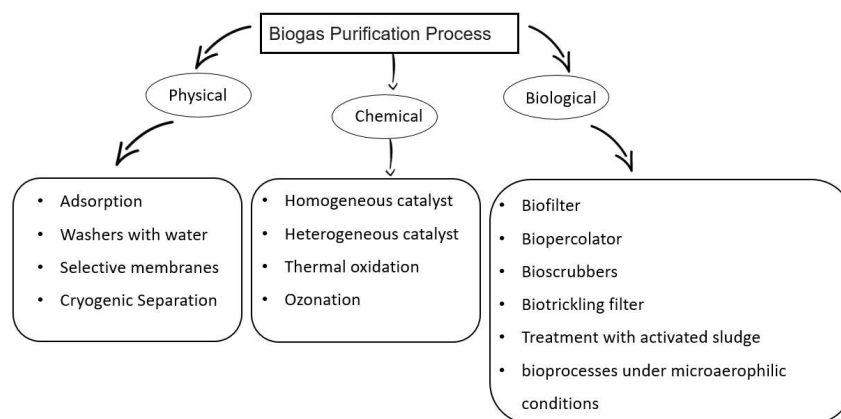


Figure 1. Biogas Purification Process.

In this sense, there is a gap in presenting the main processes that use current materials in H₂S purification techniques related to homogeneous and heterogeneous nonbiological reactive processes. This study focuses on the types of materials and processes used in H₂S purification, addressing the main advantages and disadvantages (limitations) that are found in the literature. In addition, the theme was treated through a bibliometric analysis, allowing the temporal evolution of the topic to be observed.

2. Materials and Methods

In order to present both a general and a comprehensive view of the techniques for removing H₂S from the biogas process, this study carried out a systematic literature review using the multicriteria Methodi Ordinatio methodology [22,23]. The nine steps of the Methodi Ordinatio are shown in Figure 2 [23].

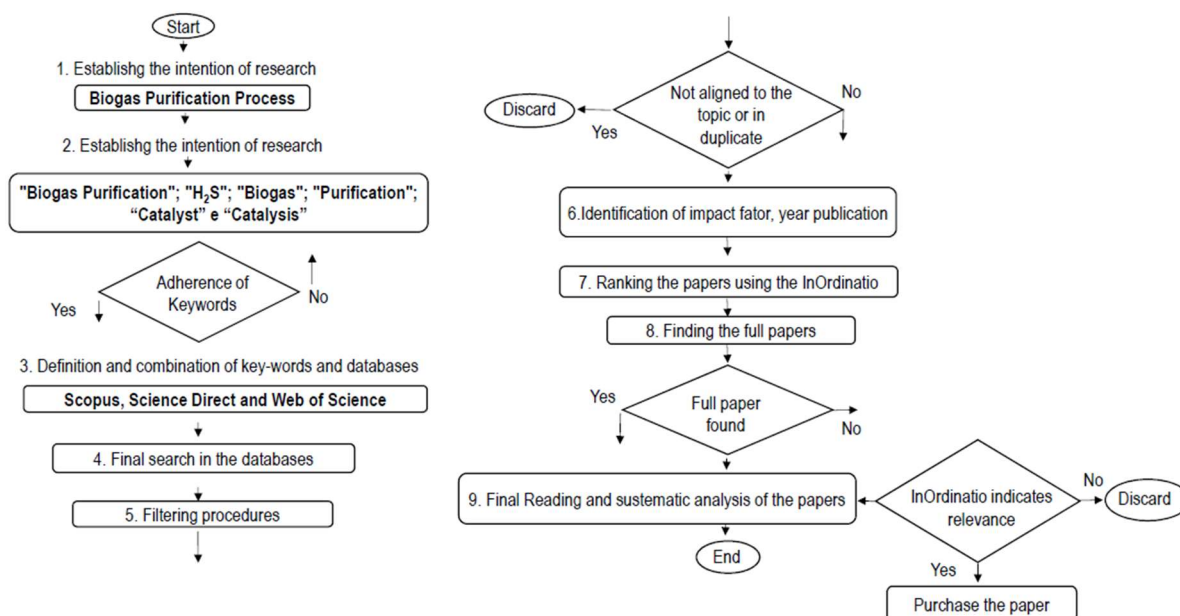


Figure 2. Steps for systematic literature review (adapted from [23]).

Keywords used in the research were: “Biogas Purification”; “H₂S”; “Biogas”; “Purify”; “Catalyst”; and “Catalysis” (Stages 1 and 2). Combinations of keywords were carried out in the final search in the databases (Stages 3 and 4). Stage 5 runs filtering procedures and eliminates duplications. Stage 6 identified the impact factor (FI), year of publication and number of Citations (Ci). In stage 7, after collecting the variables, the Equação InOrdinatio

application was conducted, resulting in a portfolio of scientific articles ordered according to Equation (1) [22,23].

$$\text{InOrdinatio} = (IF/1000) + (\alpha * (10 - \text{ResearchYear} - \text{Publish Year})) + (C_i) \quad (1)$$

where: IF (impact factor); α (value of alpha, varying from 1 to 10, to be defined by the researcher according to the importance of the novelty of the subject). For this study, the value of α was defined as 10 since the object of this study was published in recent articles recent; research year (year in which the research was developed); publish year (year in which the article was published); and C_i (number of times that the article was cited). Thus, the final portfolio, ordered by scientific relevance, included 111 articles. Stages 8 and 9 included systematic readings and analyses. After a detailed analysis of the articles, 42 articles fit the scope of this work and were selected and analyzed.

3. Results and Discussion

3.1. Bibliometric Analysis

The temporal analysis of the publications can be seen in Figure 3. A total of 111 articles had been published since 1980. The highest number of studies were published in 2022, about 15.18%, followed by 2021 and 2020 with 12.50% and 10.71% respectively. There is also an exponential growth trend of publications in the evaluated period. This demonstrates that process improvement is an object of scientific interest.

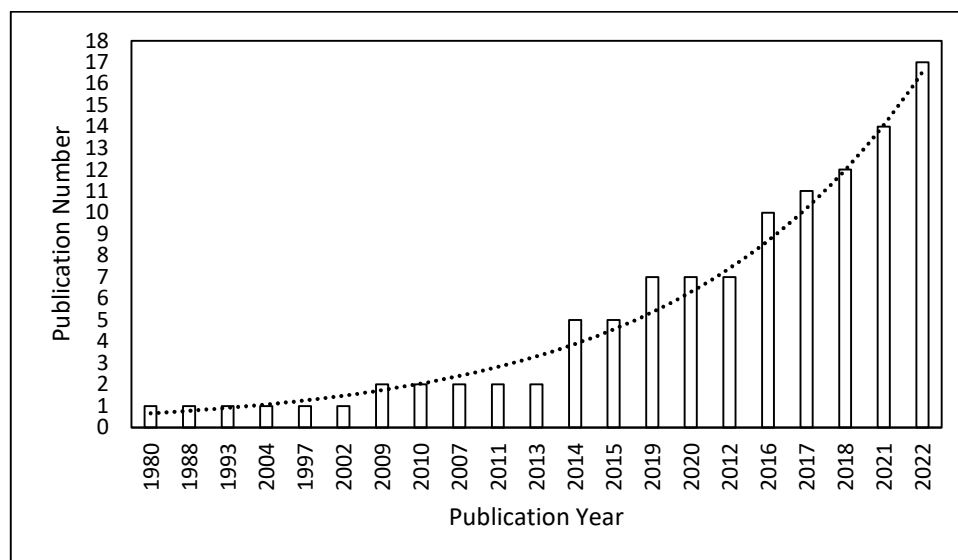


Figure 3. The development trend of studies for biogas purification. (The horizontal line indicates time, and the vertical line indicates the cumulative number of related works in each year).

The keyword analysis was performed with VOSviewer; Figure 4 the article's keywords grouped into networks. Portfolio articles contain 1382 keywords. The main keyword in the portfolio is "Biogas", with 114 occurrences in the articles; "Hydrogen Sulfate" occurs 56 times and "Biogas Purification" occurs 49 times in the articles, revealing that the themes are interconnected. The word "Desulphurization" and its derivatives also have considerable frequency. These results show that the final portfolio is aligned with the research objective, confirming the effectiveness of the methodology used.

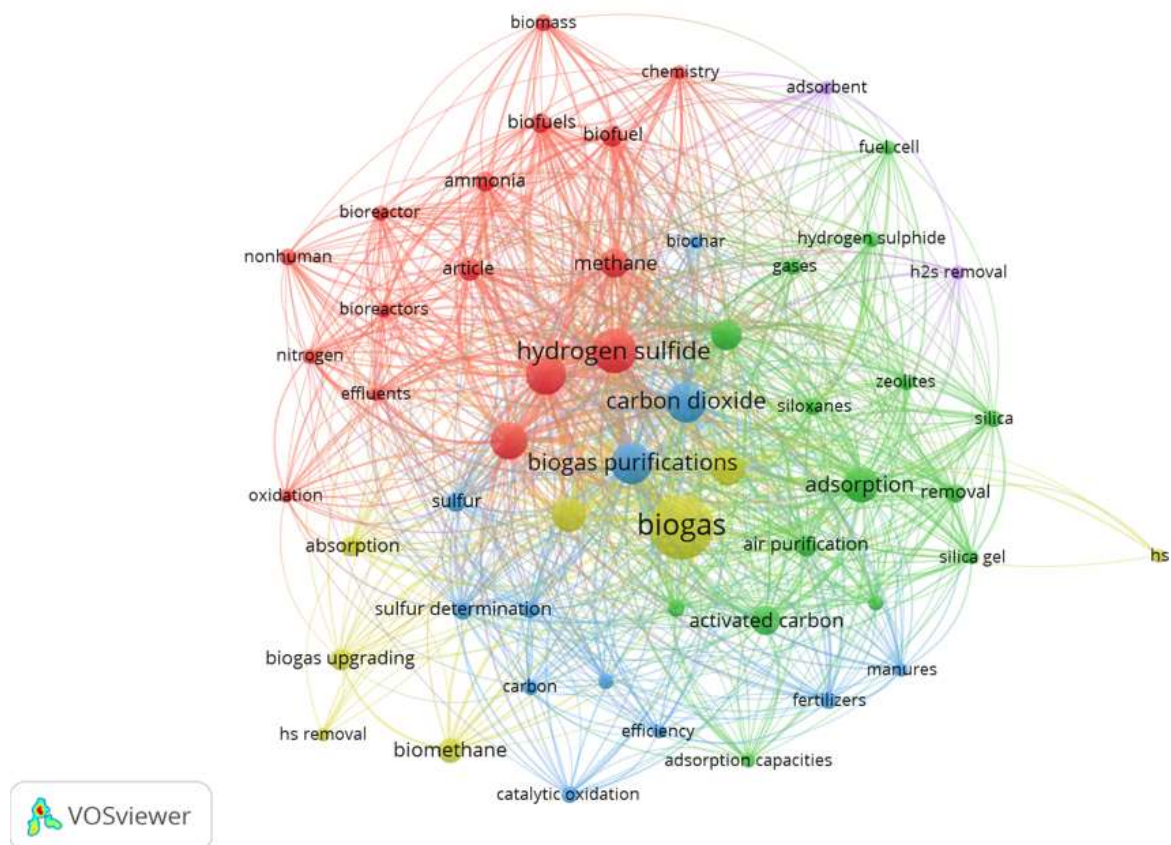


Figure 4. Main keywords.

After the bibliometric analysis, 42 articles were aligned with the study's objective. Thus, the articles analyzed in the systematic review were evaluated based on (i) type of catalyst used; (ii) main results achieved from the use of the catalyst; (iii) country where the research was applied; and (iv) limitations found in the application. From these 42 works, 8 were excluded because they were review studies, and the objective of the present study was to analyze experimental research articles. Ultimately, 34 articles were analyzed.

3.2. Homogeneous Process

Reactive and nonreactive absorption has been used both on a bench scale and on a pilot scale. Aqueous solutions are used in contact with biogas in countercurrent flow.

Biogas desulphurization can be satisfactorily achieved by chemical absorption in scrubbing towers that make use of various chemical solutions. Even simple systems, such as one composed of a single tower with NaOH as the scrubbing agent, can promote considerable reductions in the H₂S content of biogas [9,10].

Alternatively, it is possible to use of reagents that promote the conversion of hydrogen sulfide into other forms during the absorption process, making it easier to for the particulates to be recovered or disposed of. It is possible, for example, to transform H₂S into elemental S using a catalytic solution of Fe-EDTA in an absorption tower. The process is on iron chelating; H₂S is initially physically absorbed into water; it undergoes dissociation, and S is formed through sulphide oxidation by the chelated iron. The formed sulfur particles can then be separated by filtration, while the Fe-EDTA solution can be regenerated by air bubbling [8].

The sulfur produced is easily recoverable from the slurry. Another advantage of iron chelate-based processes is that they essentially operate at ambient conditions and are selective to H₂S relative to CO₂ [24].

Horikawa et al. applied such process in their study and observed a considerable increase in H₂S removal efficiency (four to five times more) in the chemical absorption (using Fe-EDTA solution) in comparison to the physical absorption of biogas (using distilled water) [8]. Lin et al., in turn, used a chemical–biological process to remove H₂S from biogas. A ferric iron solution was used to transform H₂S into elemental sulfur, which was then precipitated; at the same time, a bioreactor containing iron-oxidizing bacteria was used to regenerate the ferric iron solution. The average inlet H₂S concentration in this case was 3542 ppm. Using this system, the authors were able to achieve between 90–95% H₂S removal in a gas retention time in the range of 288–144 s [25].

When a scale-up occurred, a chemical–biological pilot system for biogas purification was built. This system consisted of three hollow absorbers in a serial connection for H₂S elimination. Regarding reactive absorption, the solution used was ferric iron sprayed out of the nozzle in the reverse direction. The system operated at 30 min per hour and 12 h, and authors reported that the results indicated in a purified biogas met the criteria of having an H₂S concentration below 150 ppm [25].

Studies involving sodium hydroxide (NaOH), calcium hydroxide (Ca(OH)₂) and monoethanolamine (MEA) indicated that the pH and the concentration of CO₂ should be considered as parameters during solution saturation. The study indicated that NaOH and MEA saturation occurred in approximately 100 min. However, the rate of saturation of Ca(OH)₂ appeared to be much faster than for the other two solutions (50 min). Since MEA has lower basicity than either NaOH or Ca(OH)₂, its rate of change in pH level was also slower. The relatively fast saturation time performed in this investigation can be attributed to how the biogas used here contained a very high concentration (47%) of CO₂ [9]. It is also worth mentioning that the solutions could be regenerated when they were saturated. In all cases, an important parameter is the proper gas-to-liquid flow ratio.

3.3. Chemisorption/Catalysis

Chemisorption/catalysis has been studied frequently regarding the removal of H₂S [14,26,27], both as the main process for removing the pollutant and combined with other removal techniques, such as absorption [28] and a polishing step. These techniques are designed to obtain very low concentrations of H₂S. Osorio and Torres' study on H₂S removal in a pilot plant, for example, included a tower containing activated carbon as the final step after a main H₂S removal process by chemical absorption in countercurrent packed scrubbers had been completed [10]. Sigot et al. studied the use of 13 X zeolite in the polishing process to remove H₂S from biogas by adsorption. They used a mixture of N₂ and H₂S with low pollutant content (80 ppm_v of H₂S), to simulate a partly desulphurized gas injected into an adsorption column containing the adsorbent. As result, it was possible to obtain H₂S concentrations below 1 ppm_v in the purified gas, a tolerable value for the use of biogas in solid oxide fuel cells -SOFCs [29].

Different types of materials with various characteristics have been used to remove sulfur compounds from biogas through adsorption/catalysis mechanisms (Table 2). Those that stand out are: activated carbon-based materials [26,29], iron oxide or iron hydroxide-based materials [26,30,31], and zeolites [12,26,29] and other semiconductors; these materials are generally known for their high adsorption capacity and selectivity.

Table 2. Materials and their H₂S removal capacity described in the literature.

Ref.	Adsorbent/Catalyst	Operational Condition	H ₂ S Removal Capacity
[32]	Activated carbon (AC)	3000 ppm _v H ₂ S, 100 mL/min, 30 °C, 1 g of activated carbon, fixed-bed reactor	1.1 L/100 g
	Steam activated AC		2.6 L/100 g
	AC impregnated with KOH		4.3 L/100 g
[33]	Cu-modified 13 zeolite (ion exchange)	8 ppm of H ₂ S in He, 0.1 L/min, 40 °C, 20 mg of sample, fixed-bed reactor	1.17 mmol/g
	Na ₂ O ₃ -AC		2.46 mmol/g
[29]	Coconut-based activated carbon	80 ppm _v of H ₂ S, 4 NL/min, 10–50 g of adsorbent	1.3 mg H ₂ S/g adsorbent
	13X zeolite		46 mg H ₂ S/g adsorbent
[34]	Biomass (wood) ash	100–600 ppm, 2.6–5.2 m ³ /h, 10.5–22.4 °C	0.56–1.25 kg/ton ash
[26]	Iron Oxide (48% wt FeOOH)	1900 ppm, 300 mL/min, 25 °C, packed reactor, 40 mm	132 mg/g
	Iron Oxide Hydroxide (48% wt FeOOH)		69 mg/g
[30]	Iron-oxide based adsorbent	600–1160 ppm _v of H ₂ S, 1200 NMm ³ /h	250–290 mg H ₂ S/g Fe ₂ O ₃
[35]	Commercial activated carbon impregnated with ZnAc ₂	700–800 ppm _v , 15 L/min–53 L/min	2.37 mg/g adsorbent
[36]	Nitrogen-doped carbon	500–1800 ppm, 15–40 mL/min, flow-bed reactor, 0.6 g of sample	48.2 mg/g
[37]	5%(wt) Cu-Activated carbon	100 ppm _v , 20 SL/h 30 °C	222 mg/g
	5%(wt) Mg-Activated carbon		242 mg/g
[38]	Zn-Fe/Al ₂ O ₃	100–250 ppm, 25 °C, 2.5 g of adsorbent	3.23 mg/g adsorbent
[39]	Coconut activated carbon samples impregnated with ZnAc ₂ and TiO ₂	5000 ppm, 5.5 L/min, 1 bar, 30 °C	1.92 mg/g

Activated carbons are already widely known as adsorbents and have been studied for their H₂S removal potential. Some comparative studies highlight the superior performance of ACs in the removal of hydrogen sulfide [33], while other studies have indicated that pure ACs do not always present the best results in H₂S removal [26,29]. However, AC samples can be modified to improve their H₂S removal capacity.

Sitthikhankaew et al., for example, upgraded AC samples by steam activation and impregnated them with KOH. It was observed that KOH impregnation considerably increased the H₂S adsorption capacity, breakthrough time and adsorption time of the samples. After impregnation, adsorption capacity increased from 1.1 L/100 g in unmodified AC to 4.3 L/100 g in the KOH impregnated AC. In upgraded samples, the capacity increased from 2.6 L/100 g to 3.0 L/100 g after impregnation. This improvement, according to the authors, was caused by a combination of the reaction between H₂S and KOH and physical adsorption. First, hydrogen sulfide was adsorbed in the AC surface; then, it reacted with KOH, forming KHS and K₂S. Regarding steam activation at 900 °C, it was observed that the process had a strong impact on the increase in surface area and pore volume, from 1343 m²/g and 0.45 cm³/g in AC to 1621 m²/g and 0.60 cm³/g in the upgraded AC. This transformation resulted from the increase in the material porosity promoted by the partial burn off of the material during the steam activation process [32].

Micoli et al. in a comparative study, impregnated AC samples with NaOH, KOH and Na₂CO₃. The obtained results revealed that AC-Na₂CO₃ presented the best performance with the longest breakthrough time and the slowest increase in H₂S concentration in the output [33].

Cimino et al. prepared ACs impregnated with Cu and/or Zn and observed that the simultaneous presence of water and oxygen favored H₂S removal rate and adsorption capacity increase. This behavior was most notable in samples containing Cu, resulting in additional formation of elemental sulfur and organic sulfur [40].

Cepollaro et al. in turn, found that loading of Cu and Mg in activated carbon honeycombs considerably favored the removal of H₂S. Data presented by the authors indicated an increase in adsorption capacity from 0.5 mg/g for AC in 0.4 h to 222 mg/g and 242 mg/g for samples containing 5% wt of Cu and 5% wt of Mg in 96 h and 56 h, respectively. Furthermore, analyses carried out by the authors suggested that, even though the faster removal promoted by the presence of Mg led to a greater production of elemental sulfur, Cu promoted deep oxidation along with the formation of both sulfates/sulfuric acid and elemental S. [37].

Based on a response surface methodology (RSM), Zulkefli et al. optimized parameters of ZnAc₂ impregnation in commercial activated carbon, which allowed a specific surface area equal to 620.55 m²/g and an H₂S adsorption capacity equal to 2.37 mg/g [35] to be obtained. Later, Zulkefli et al. produced coconut activated carbon samples impregnated with ZnAc₂ and TiO₂ that showed increasing H₂S adsorption capacity with increasing temperature (1.67 mg/g, 1.84 mg/g and 1.96 mg/g at 50 °C, 100 °C and 150 °C, respectively) [39].

Iron-based materials are very promising for H₂S removal; in many cases, they obtain better results than materials such as activated carbon [26,41]. This class includes materials such as iron oxides and iron hydroxides, and stands out for being able to react with adsorbed H₂S, facilitating its removal [26].

In the work by Bak et al. iron-based materials showed superior performance in H₂S removal compared to activated carbon, silica gel or zeolites-based materials, due to their ability to promote chemisorption reactions that favor H₂S adsorption. Both the iron oxide (61% wt Fe₂O₃) and the iron oxide hydroxide (48% wt FeOOH) tested by the authors showed high adsorption capacities (69 mg/g and 132 mg/g, respectively), with the surface area being a determining factor for performance difference between the two (77 m²/g and 125 m²/g, respectively). The superiority of these materials is evidenced by comparing their specific area with that of the activated carbon tested by Bak et al. (1007 m²/g), which, despite having a larger surface, did not present as good a result as the iron-based materials [26].

The iron-oxide based adsorbent used by Zhang et al. presented an adsorption capacity around 0.25–0.29 g H₂S/g Fe₂O₃. In a dry desulfurization filter containing the adsorbent, almost complete H₂S removal from the biogas was possible within 40 days, but operating conditions were not very suitable for industrial purposes (packed layer height equal to 1 m, operating at 0.014 m/s) [30].

Farghali et al. studied the direct addition of waste iron powder (WIP) and iron oxide nanoparticles (INPs) to batch biodigesters in order to improve CH₄ yield and reduce H₂S production inside the reactor [31]. Both additives presented good performances in the H₂S control, especially WIP, which achieved 77.24% H₂S reduction when used at a concentration of 1000 mg L⁻¹.

3.4. Zeolites

In the comparison of three different adsorbents (coconut-based activated carbon, VWR BDH Prolabo silica gel and 13X zeolite), Sigot et al. observed that the zeolite presented the best performance in the H₂S adsorption. The authors noticed that there was no direct relationship between this result and the textural properties of the material, such as its specific surface area or pore volume, indicating that H₂S adsorption is highly specific. Potential explanations include the alkaline characteristic of the zeolite studied (leachate pH close to 10) and the catalytic activity of aluminum and sodium present in the material, which enable a mechanism of “adsorption–dissociation–oxidation”, similar to what occurs with activated carbon. The experiments carried out by the authors also made it possible to identify internal diffusion as the limiting step in the process (Sigot et al., 2016).

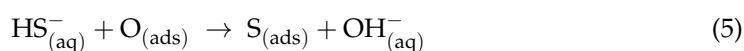
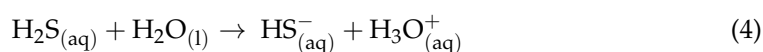
In another work, Sigot et al. deepened their study on the H₂S retention mechanism in zeolites and the adsorbent regeneration process [12]. Zeolite characterizations, before and after H₂S adsorption, indicated low desorption at 350 °C, suggesting that this was not a physical adsorption process. The results also confirmed the occurrence of an adsorption–desorption–oxidation mechanism that involved the formation of elemental sulfur.

According to Micoli et al., the presence of cations such as Na⁺, K⁺, Ca²⁺ or Mg²⁺, common in zeolites, can contribute to H₂S chemisorption by promoting acid–base reactions [33]. In addition, as highlighted by Sigot et al., other metals present in zeolites, such as aluminum, sodium, iron, magnesium and calcium, even in very low concentrations, can act as catalysts, so their contribution to H₂S removal cannot be neglected [12]. Thus, it is possible to further improve zeolites' performance through the addition of metal ions. In this sense, Micoli et al. observed the improvement in 13X zeolite performance after Zn or Cu addition. For the authors, the basic oxides CuO and ZnO that were formed in the zeolite react with H₂S and favor its removal [33]. Bahraminia et al. also observed an improvement in NaA zeolite after Ag impregnation, increasing its H₂S adsorption capacity to 3.24 mg /g and achieving 310 min of breakthrough time [42].

In addition to zeolites, other oxides have also been applied to H₂S removal. Normally, they are materials used in the selective oxidation of H₂S, focused on the conversion of H₂S to elemental S and on the prevention of reactions such as deep oxidation to SO₂, which are undesirable [14,27]. Ruiz-Rodrigues et al. applied Cu-promoted V₂O₅ catalysts in H₂S oxidation and observed low SO₂ formation for all tested catalysts and selectivity to elemental S higher than 95% when H₂S conversion was under 90% [27]. Lee et al. used a V₂O₅-TiO₂ catalyst synthesized by sol-gel/hydrothermal methodology in the selective oxidation of H₂S to S, obtaining good results with significant influence of the H₂S/O₂ ratio and temperature [14]. It is also possible to employ photocatalytic processes for H₂S removal, as performed by Hao et al., who used a zeolite–TiO₂ mixture for selective photocatalytic conversion of H₂S into S. By combining zeolite and titanium dioxide, the authors achieved H₂S conversions of up to 97% and SO₂ selectivity of only 9.2% [43].

3.5. H₂S Removal Mechanisms

Sigot et al. in the study about the removal mechanism of H₂S by zeolites, suggested the occurrence of a mechanism of adsorption–dissociation–oxidation [12], similar to other mechanisms proposed for adsorption on activated carbon. The proposed mechanism starts with the adsorption of the hydrogen sulfide present in the gas (Equation (2)), followed by H₂S dissolution (Equation (3)) and dissociation (Equation (4)) in the water film present in zeolite pores. Then, still according to the authors, HS[−] generated is oxidated by adsorbed oxygen (Equation (5)), forming elemental sulfur which can further lead to the formation of cyclic or linear sulfur polymers (Equation (6)) [12]:



Thus, the overall equation proposed by the authors is [12]:



That said, the validity of the mechanism proposed by Sigot et al. is reinforced by the results obtained by Sitthikhankaew et al. in their study that addresses how the presence of O₂, H₂O or CO₂ affects H₂S removal. Sitthikhankaew et al. observed that the presence

of oxygen considerably favored hydrogen sulfide removal when either unmodified AC or AC impregnated with KOH were applied. The oxygen addition to the system favors the oxidation reaction (Equation (7)), promoting the H₂S conversion to elemental S and water formation.

Addition of water (humidity) also improves H₂S removal, increasing adsorption capacity and adsorption time. This is because, at higher relative humidity, H₂S can more easily dissolve in water film and dissociate into HS[−] and H⁺, as shown in Equation (3). In the comparison between the effects of O₂ and humidity, Sitthikhankaew et al. noticed that oxygen addition is more effective in improving adsorption at low H₂S concentrations, while humidity is better at improving adsorption at higher H₂S concentrations [32]. In a similar way, Cimino et al. observed that the simultaneous presence of O₂ and H₂O had a notable positive effect on the removal of H₂S in tests involving ACs impregnated with Cu [40].

Curiously, the presence of humidity sometimes seems to have a negative effect on the removal of H₂S in the case of iron-based materials, as demonstrated by the work of Cristiano et al., who observed a drastic reduction in the breakthrough time when water-saturated gas was used in H₂S removal tests with α-Fe₂O₃ [41]. Moisture in the gas also had a negative impact on H₂S breakthrough time in tests using Zn-Fe/Al₂O₃ [38].

The presence of CO₂, in turn, presented a negative effect on H₂S adsorption, probably due to the competition between CO₂ and H₂S for adsorption sites [32].

In addition to elemental sulfur, the authors have already proposed the formation of other sulfur compounds as a result of reactions that occur during the removal process. In their study on H₂S capture by biomass ashes, Juárez et al. proposed the formation of polysulfides and S₈ due to the occurrence of secondary reactions that led to the consumption of hydrogen sulfide [34]. Cepollaro et al., in turn, noted that AC samples modified with Mg led almost exclusively to the formation of elemental S chains, while samples containing Cu also produced sulfates and sulfuric acid in addition to elemental S [37].

Cations commonly present in zeolites may also play an important role in H₂S removal. Sodium, for example, can promote acid–base reactions with H₂S (Equation (8)), contributing to its chemisorption; this is similar to other cations present in zeolites (potassium, calcium, etc.) [33]:

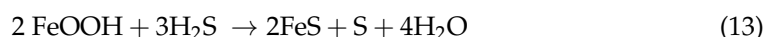
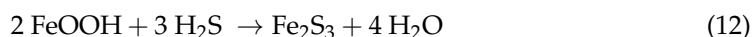
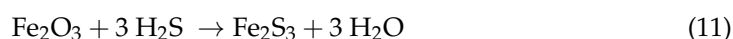


It is also necessary to consider the reactions of H₂S with other metals and their oxides, such as CuO (Equation (9)—[33]), ZnO (Equation (10)—[33,38]),

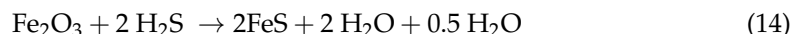


Cimino et al. proposed two possible pathways for the reactive adsorption mechanism of H₂S in CuO-ZnO/activated carbons: the first involved the reaction between H₂S and lattice oxygen that is present in metal oxides clusters or other superficial species to produce metal sulphates; the second involved the H₂O and O₂ present in the gas to catalytically produce elemental S or organic sulfur. The two pathways can occur either simultaneously or sequentially, with the first being faster than the second [40].

It is commonly known that iron-based materials, i.e., those which are predominantly composed of iron oxides or iron hydroxides, are capable of promoting chemisorption reactions and the formation of elemental sulfur. Such processes can be exemplified by the reactions between H₂S and Fe₂O₃ (Equation (11)) and between H₂S and FeOOH (Equations (12) and (13)) [26]. It is necessary to consider the low breakthrough time represented by samples of the type studied by Bak et al. [26].



Yan et al. also proposed another possible reaction between Fe_2O_3 and H_2S [38]:



3.6. Limitations in the Materials Application

All processes found in this review had both positive and negative points. Reactive absorption is complex, however the solution used is often easy to regenerate. However, it has many disadvantages, such as needing an additional process to separate elemental sulfur, energy to regenerate the solutions, stability, formation of biofilm or ferric hydroxide resulting in clogging, high corrosion rate and sizing of the columns [25].

In processes with heterogeneous catalysts, many issues in terms of technological maturity and economic viability need to be addressed before the process can be exploited on an industrial scale. Issues that exist include catalyst deactivation and regeneration as well as efficient H_2S removal.

Authors have studied various materials and reported the difficulties they encountered. In the opinion of Peluso et al. (2019), amino-functionalized ordered mesoporous silicas have produced very interesting results, both in terms of adsorption performance and regeneration capacity, but are not widely tested in large-scale “real-life” applications and deserve further investigation, in particular for H_2S and CO_2 discrimination [44]. At the same time, despite very good results in studies, there are few works that deal with the adsorption of H_2S in metallic nanoporous organic structures.

In the work by Bareschino et al. (2020) the experimental results show that complete saturation of the bed could never be achieved, since the H_2S output concentration approaches an asymptotic value that is always lower than the input one, and as a consequence, there were catalytic oxidation reactions of the sulphide hydrogen [45].

For Kaplan et al. (2021), adsorption on modified activated carbon in a desulfurization bed can be an economic problem. The price, in comparison with other desulfurization beds available on the market, can be a disadvantage; however, it has excellent H_2S absorption efficiency. Therefore, there must be a longer use time for the cogenerator, which would allow for delayed replacement of used components [28].

In the work developed by Zulkefli, et al. (2021), based on the adsorption–desorption cycle, it was observed that the adsorbent degraded slightly; the H_2S adsorption capacity was calculated up to 16% and 23% for optimized and nonoptimized adsorbents, respectively, over the years’ cycles. It is suggested that the degradation could be due to insufficient desorption process, i.e., nonoptimized conditions, and probably because of the complex mechanisms that occur during the adsorption–desorption process. Thus, comprehensive studies are needed in the future to analyze the degradation of the adsorbent by optimizing the conditions of the desorption process and to analyze the mechanism of adsorption–desorption of H_2S in the adsorbent [35].

Bimetallic adsorbent materials based on the commercial coconut activated carbon (CAC), surface-modified with metal acetate (ZnAc_2) and metal oxide (ZnO and TiO_2) that Zulkefli et al. (2022) studied indicated that humidity affected the adsorption capacity for hydrogen sulfide gas [39].

Dong et al. (2022) used a desulfurization method involving natural amino acid salts (ASA) and described parallel adsorbent modules operated in an adsorption–regeneration configuration. However, the study indicated that the high cost of regeneration and adsorbent material limited the method’s application in small-scale digestion [46].

4. Conclusions

Biogas purification, and H_2S removal in particular, is a very relevant topic, both for the enrichment of biogas energetic potential and the mitigation of its harmful and polluting effects caused by its corrosive and dehydrating power. In industry, to avoid compromising the life of equipment (mechanical components) hydrogen sulfide (H_2S) must

be removed. This removal can be advantageous for the generation of electricity as it can increase motor efficiency.

In this context, there was an exponential increase in the number of publications related to this topic. A wide range of physical, biological and chemical processes have already been studied for this purpose. Focusing on chemical processes, many of the processes mentioned can be indicated as catalytic, such as reactive absorption (homogeneous catalysis) and the use of adsorbents modified with metals (heterogeneous catalysis) acting as promoters. There is a wide range of materials used for H₂S removal, in particular activated carbons, zeolites and iron-based materials, both pure and modified. Studies demonstrate that these materials can act by different mechanism pathways, notably reacting with H₂S to form elemental sulfur, organic sulfur and metallic sulphates, among others. Catalytic routes have focused on the selective oxidation of H₂S to form elemental S, avoiding deep oxidation to SO₂, which is also a pollutant.

The analysis of the processes performed in this work, allowed the identification of advantages and disadvantages, being important the continuous study of the subject. The chemical processes that were the focus of this work, such as chemisorption and both homogeneous and heterogeneous catalysis, proved to be very promising as they allow the conversion of H₂S into elemental sulfur. Among the heterogeneous processes, the use of adsorbents, such as AC and zeolites, modified by the addition of metals seems to be very promising for better conversion of H₂S. In addition, the aforementioned processes stand out for allowing the regeneration and reuse of catalysts and reagents, reducing costs for the process. However, precise regeneration and reuse, along with other parameters, require further studies to enable their application on an industrial scale.

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