Recent Attempts on the Removal of H₂S from Various Gas Mixtures Using Zeolites and Waste-Based Adsorbents

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Abstract: Natural gas, biogas, and refinery gas all include H₂S, which has adverse effects not only on the environment and human health but also on the equipment and catalysts that are employed in the relevant processes. H₂S is removed from the aforementioned gases using a variety of techniques in order to fulfill the necessary sales criteria and for reasons of safety. The adsorption method stands out among various other approaches due to its straightforward operation, high level of efficiency, and low overall cost. This technique makes use of a variety of adsorbents, such as metal-organic frameworks (MOFs), activated carbon, and zeolites. The use of zeolite-based adsorbents is by far the most common of these various types. This is due to the specific properties of zeolite-based adsorbents, which include a high adsorption capacity, the ability to be regenerated, a high temperature stability, a diversity of types, the possibility of modification, high efficiency, and low cost. In addition, research is being done on adsorbents that are made from inexpensive raw materials in order to remove H₂S. This article focuses on zeolites, zeolite modifications, and wastes as an adsorbent for the removal of H₂S, all of which have been investigated fruitfully in recent years, as well as the promising applications of zeolites.

Keywords: H₂S removal; separation; zeolites; zeolite synthesis; adsorption; adsorbents; waste derived adsorbents; adsorption capacity

1. Introduction

Crude oil, natural gas, coal, and biogas are the primary forms of energy resources on the planet. There is an ever-increasing demand for these fuels, and governments are implementing policies to reach zero emissions. The presence of various toxic substances in these fuels leads to the release of harmful substances into the environment during their use. Therefore, fuels are tested to meet certain standards before use. According to the International Energy Agency, natural gas accounts for more than 23% of the world's fuel supply. Natural gas contains a number of various gases that are toxic, such as H₂S, mercaptans, and disulfides. Natural gas and biogas both contain varying amounts of hydrogen sulfide, and because of its corrosive and toxic qualities, they both need to be purified. Natural gas may have varying quantities of H₂S in order to satisfy regulatory criteria. For instance, the standards for a pipeline allow for up to 5 ppm in European countries [1], while in the United States it is only 4 ppm [2].

Techniques such as adsorption, absorption, cryogenic distillation, and membrane processes are utilized most frequently in order to bring the amount of H₂S to an acceptable level. Each approach comes with its own set of benefits and drawbacks; the one chosen will depend primarily on the concentration of H₂S present in the mixture as well as the price of the adsorbent or absorbent used in the process. Because of its low cost, high level of safety, and numerous other advantages, adsorption is by far the most popular approach. It

makes use of a wide variety of adsorbents, including as metal-organic frameworks (MOFs), activated carbon, and zeolites, and new combinations of these adsorbents are continually being produced and examined.

Although there have been a number of qualitative review studies [3–7] devoted to the theoretical and experimental separation of H_2S on the different types of adsorbents, such as zeolites, activated carbon, MOFs, oxides, and so on, there is still a lack of consensus regarding the best method. This article focuses on the experimental removal of H_2S from natural gas, biogas, air, and refinery gases in the past decade utilizing zeolites, zeolite-based adsorbents, and waste-based adsorbents. We have only tried to concentrate on the part of the research that deals with the outcomes of experiments, in contrast to other researchers who have researched both theoretically and empirically.

Because the researchers stated the adsorption capacity of the materials in a variety of units, including mmol/g, μmol/g, and mg/g, we had to recalculate all of the units into mg H_2S/g in order to make accurate comparisons. However, since several works expressed adsorption performance in percentages (which is impossible to convert into mg H_2S/g due to a lack of data) rather than the adsorption capacity or the efficiency of the adsorbent, we have provided adsorption performance in the same way.

1.1. Measurement of Hydrogen Sulfide Concentration

The concentration of H_2S is one of the most crucial quality standards for natural gas and biogas. Therefore, it is determined using a variety of techniques. Cost, application complexity, and measurement precision all vary amongst them. As a result, several techniques are employed for various goals. Standards for accurate measurements have been developed and registered by international organizations such as ASTM, UOP, and GPA [8]. The following approaches have been employed in lab settings in numerous research studies because they are straightforward to use despite the complexity of these basic test methods.

1.1.1. Gas Chromatography

One of the most accurate methods for identifying the precise concentration of the individual components that comprise a mixture is the use of gas chromatography. Measurement of the signals that are produced by the components of the sample that are separated in the column is the basis for this method. Porous polymers, such as Poropack [9], Hayesep-Q column, and sulfur chemiluminescence detector (SCD) [10], are utilized as GC column materials. This method is utilized for doing exhaustive compositional analysis [8].

1.1.2. Analyzers

Analyzers are readily accessible for purchase in the marketplace and have found widespread application [11,12] to monitor or identify certain gases for a number of applications. The following are some of the most prevalent H_2S measurement methods that were utilized in the development of the analyzers. These devices are based on a number of different methodologies.

Electrochemical

Detectors are utilized largely for the purposes of personnel protection and providing information regarding pollution in the workplace. Nevertheless, as can be seen from the numerous studies that have been reported in the literature [13,14], detectors were utilized to measure the concentration of H_2S for the sake of research as well. In the electrochemical detectors, the release of free electrons and a decrease in the resistance between the two electrodes occur when H_2S molecules take the place of oxygen molecules. This change, which may be detected immediately, is directly proportional to the amount of H_2S that is present in the gas. On a lab scale, the H_2S concentration can be measured in a variety of ranges, from 0 to 1000 parts per million (ppm), using electrochemical sensors. Although this kind of instrumentation is readily available in both portable and fixed-point solutions and has the potential to be useful in measuring H_2S, it is not without

drawbacks. Electrochemical cell-based sensors need to be calibrated frequently. They are also susceptible to high temperatures, high humidity, low oxygen levels, and other conditions that might cause drift and cell degradation.

Lead Acetate

H_2S tape analyzers make use of a tape that has been coated with lead acetate in order to detect the presence of H_2S in a gas sample. This detection method is predicated on the reaction that takes place between H_2S and lead acetate, which results in the formation of lead sulfide. There is a direct correlation between the amount of H_2S present and the darkness of the stain on the type. These tape analyzers have the capability of accurately measuring low levels of H_2S, despite the considerable initial investment required to purchase one. Despite having portable possibilities, this kind of analyzer is often stationary. The interference from SO_2 and both low and high humidity can affect the lead acetate tape.

Tunable Diode Lasers

Tunable diode lasers (TDL) are frequently utilized in the process of measuring the concentrations of the constituents of the gas. The absorption properties of different gases are utilized by the technology so that the concentration of a target gas can be accurately measured. After traveling through the gas sample, the laser light's intensity is measured by a detector so that the target gas concentration can be derived from this information. Measurements that are exact and exceptionally dependable can be produced by a correctly built TDL analyzer even when the concentration of H_2S present is very low.

1.2. Physicochemical Properties of the H_2S

Hydrogen sulfide is a colorless and flammable gas that has a strong and distinctive odor of rotten eggs. It is also known as hydrosulfuric acid, sewer gas, stink damp, dihydrogen monosulfide, dihydrogen sulfide, sulfane, sulfurated hydrogen, and sulfur hydride. It has a greater density than air and may settle on the ground. The characteristics of H_2S that are most important to know are outlined in Table 1.

Table 1. Chemical and physical properties of H_2S [15].

Properties	Value
Molar mass	34.081 g/mol
Specific gravity	1.2
Boiling point	$-60.33\,°C$
Melting point	$-85.49\,°C$
Smell	Rotten eggs
Color	Colorless
Density	1.5392 g/L at STP
Solubility in water	$4\,g\,dm^{-3}$ (at $20\,°C$)
Lower Explosive Limit	4.3%
Upper Explosive Limit (UEL):	45%
Autoignition Temperature:	$270\,°C$
Vapor Pressure:	1880 kPa at $20\,°C$
Vapor Density (Relative to Air):	1.189
Kinetic diameter	0.36 nm

1.3. Adsorption of H_2S

The term "adsorption" refers to a process in which specific compounds are selectively retained by the formation of a physical bond with a solid surface known as an "adsorbent." Certain gases are drawn to solid surfaces due the attraction exerted by Van der Waals forces and hydrophobic interactions. The bonding energies involved in adsorption fall somewhere in the range of 10 to 70 kJ/mol [16]. If the adsorbent can be regenerated, adsorption is an energy-efficient process because it allows the adsorbent to be reused multiple times during the adsorption–desorption cycle.

A number of different adsorbents, including metal oxides [17–19], metals [20], metal-organic frameworks [21], zeolites, and carbon-based materials [22], are utilized in the process of removing hydrogen sulfide from a gas mixture that also contains CH_4, CO_2, N_2, and H_2. For an adsorbent to be effective in the process, it needs to have a high adsorption capacity, the ability to be regenerated, the ability to maintain its stability at high temperatures, and a high selectivity for the molecule that needs to be removed. Adsorption of H_2S is often performed in a fixed bed adsorption column when it is done on a small scale, such as in a laboratory (see Figure 1).
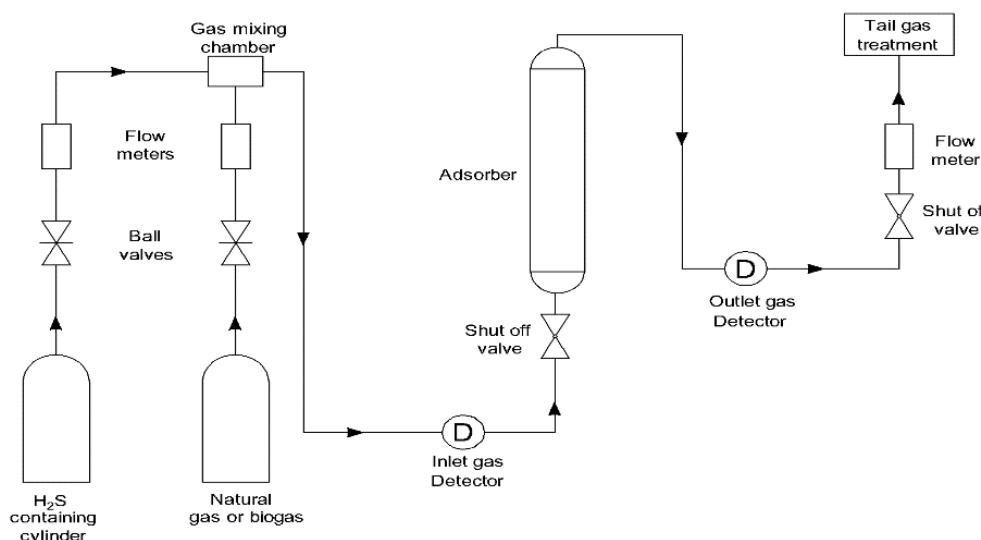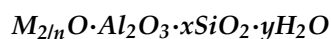

Figure 1. Typical experimental laboratory setup for the removal of H_2S.

1.4. Zeolites

Zeolites are crystalline solids formed by the systematic interaction of tetrahedral molecules of AlO_4 and SiO_4. The following empirical formula can be used to represent them:

$$M_{2/n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$$

Because AlO_4 tetrahedra are only linked to SiO_4 tetrahedra, *x* in this oxide formula is usually equal to or greater than 2, and *n* is the cation valence. The cation and water molecules are accommodated in the framework's channels and linked spaces. The cations are very mobile and may generally be exchanged with other cations to variable degrees.

According to the International Zeolite Association [23] there are more than 40 natural and more than 280 zeolites that have been artificially synthesized. These zeolites are distinguished from one another by their unique crystal structure and the ratios of Al and Si atoms. In the zeolite molecule, the Al atom is negatively charged and can be balanced with cations such as Na^+, K^+, and Ca^{2+}. Zeolites have pores that allow molecules of a lower diameter to be adsorbed, whereas molecules of a larger diameter are unable to pass through these pores. This is an attractive adsorptive property for removing impurities such as hydrogen sulfide, carbon dioxide, and moisture from natural gas. To this day, a large number of zeolites have been synthesized and evaluated for the separation of H_2S from a wide variety of mixed gases, and the findings have been very encouraging.

The zeolites known as Faujasite (FAU) and Linde Type A (LTA) are utilized rather frequently in the separation processes. They are composed of sodalite (SOD) structures that are organized in a pattern that varies depending on the amount of aluminum to silicon (Figure 2).
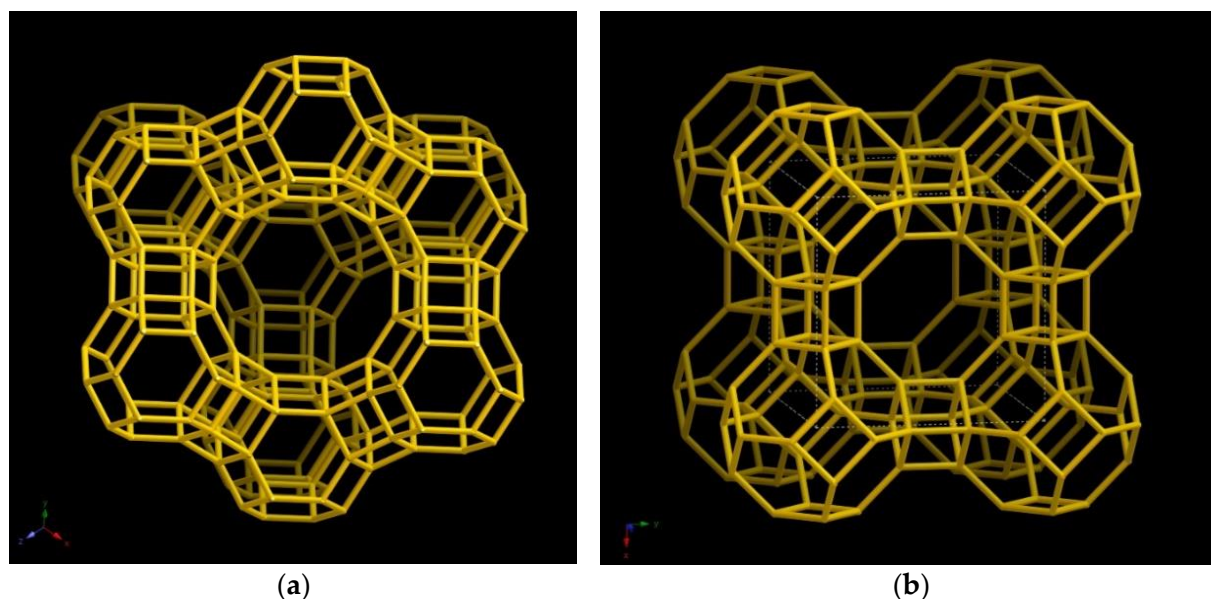
(a)   **(b)**

Figure 2. Structure of (**a**) Faujasite (FAU) and (**b**) Linde Type A (LTA) zeolites [23].

1.5. The Synthesis of Zeolites

Natural zeolites can be found in large quantities all over the world, but they are not commercially available because of their low purity, the high cleaning cost, and inability to be used in certain processes. Synthetic zeolites, on the other hand, are produced on an industrial scale. These zeolites serve as adsorbents, catalysts, and ion-exchangers, among other functions, and are utilized for a variety of applications. Milton [24] developed the first low-silica zeolites in the late 1940s by hydrothermally crystallizing alkali aluminosilicate gels under low temperatures and pressures. Synthesizing zeolites can be done in a number of different ways, including the hydrothermal [12], alkali-fusion [25], and microwave-assisted [26] methods. The synthesis of an appropriate zeolite can be accomplished using any one of the aforementioned approaches. As raw materials, a variety of salts and minerals containing the elements aluminum and silicon are utilized. The elements aluminum and silicon can be obtained from a variety of sources, including sodium aluminate, aluminum sulphate, aluminate nitrate, sodium, or alkaline silicate, and minerals such clay and kaolin [27]. The synthesis of an appropriate zeolite can be accomplished using any one of the aforementioned approaches. As raw materials, a variety of salts and minerals containing the elements aluminum and silicon are utilized. The elements aluminum and silicon can be obtained from a variety of sources, including sodium aluminate, aluminum sulphate, aluminate nitrate, sodium, or alkaline silicate; minerals such clay and kaolin [28]; and from iron ore tailings, rice husk ash, coal fly ash, lithium slag, and paper sludge ash.

1.6. H_2S Adsorption Mechanism on Zeolites

There are two primary explanations for why H_2S can be absorbed physically by zeolites:

- One of the things that sets zeolites apart from other minerals is the fact that their chemical structure remains relatively unchanged throughout time. These particular chemical structures have pores that are on the nanometer scale, and they appear to function as molecular sieves. Even molecules that are significantly smaller than the pores found in zeolites have the potential to become "trapped" within these pores. In light of this, it is possible to estimate the zeolite that can be employed [29] by first determining the kinetic diameter of the molecule that needs to be separated. Zeolites with pore sizes larger than 0.36 nm, which is the kinetic diameter of H_2S, have the ability to adsorb H_2S. Presence of impurities such as CO_2, which has a kinetic diameter of 0.33 nm, cause a low separation efficiency due to competitive adsorption. Table 2

provides the kinetic diameters of several molecules that could be present in the mixture with H_2S and induce competitive adsorption.

Table 2. Kinetic diameter for various molecules [29].

Molecule	Kinetic Diameter (nm)
NH_3	0.26
H_2O	0.28
CO_2	0.33
N_2	0.36
O_2	0.36
SO_2	0.36
CH_4	0.38

- The second explanation is that zeolites are able to adsorb H_2S as a result of contact with the polar structure of the zeolite [30]. When the intracrystalline pores and channels of zeolites are filled with H_2S molecules, the zeolites are unable to adsorb, and there are no more adsorptions that take place. It is possible to restore the adsorption capacity of zeolite by modifying the conditions of the adsorption equilibrium [31] in terms of temperature, pressure, or both. This process is referred to as "regeneration". The contact between the molecules being adsorbed and the active sites (sites placed over the external surface of the zeolites, or close to the micropore openings) of the zeolite becomes less strong with time, which results in the molecules being desorbed. During the adsorption process, the permanent structure of the zeolites is maintained since the phase of H_2S that is adsorbed onto the zeolites does not change any of the zeolites' atoms. Temperature, pressure, and polarity are the three most important factors that determine how well H_2S can be adsorbed.

Sometimes, chemical bonds such as covalent or ionic are formed between the surface of the zeolite and H_2S. This process is known as chemisorption, and its interaction is much stronger than physisorption. Chemisorption can, in fact, meet the demand for the selective capture of H_2S; however, one drawback is that it results in the development of irreversible bonds, which reduces the potential for regeneration. Therefore, for H_2S separation in industrial processes, physisorption is preferred, as the reversible process take place by weak van der Waals forces and electrostatic interaction.

1.7. The Effect of Si/Al Ratio on H_2S Adsorption

The ratio of silicon to aluminum, which is known as the Si/Al ratio, is the most significant factor in determining the structures and properties of zeolites. Zeolites can be categorized as low, medium, high, or silica, depending on this ratio [32]. The thermal stability, acidity, and structural makeup of zeolites are all influenced by the Si/Al ratio. When the ratio of silicon to aluminum increases, some properties, such as thermal stability, increase. The amount of silica found in hydrophilic zeolites is quite low, whereas the amount of silica found in hydrophobic zeolites is relatively considerable [5]. Ion exchange capacity and cation concentration are both influenced by the amount of aluminum present, and both tend to decrease as the ratio of silicon to aluminum rises. For the purpose of separating hydrogen sulfide from a variety of streams, hydrophilic zeolites with a high level of surface selectivity are recommended. In this case, zeolites of types A and X that have a low silica content and demonstrate strong adsorption capabilities are preferable candidates. Karge and Rasko [33] investigated how the ratio of silicon to aluminum influences the mechanism of hydrogen sulfide adsorption by the FAU zeolites (X and Y). When the ratio of silicon to aluminum was larger than 2.5 (Y), they discovered that physical adsorption of H_2S occurred. Due to the fact that low silica zeolites (Si/Al = 1–1.5) are aluminum saturated and have the largest cation concentration, it may be deduced that Na^+ cations play an important role in the dissociative adsorption. Consequently, an increase in the Si/Al ratio causes a decrease in the amount of Na^+ ions, which in turn causes a decreased dissociation of H_2S

into HS⁻ and H⁺, indicating an increase in physical adsorption. Moreover, replacing the Na⁺ cations in a 4A zeolite with Ca^{2+}, a 5A zeolite is produced, resulting in an increase in pyhsisorption [34]. The Si/Al ratio of zeolites, which are frequently employed in separation processes, is shown in Table 3 below:

Table 3. The Si/Al ratio of zeolites [29].

Type of the Zeolites	Si/Al Ratio
Linde type A (LTA)	1–6
Faujasite X type	1–1.5
Faujasite Y type	higher than 1.5
Chabazite (CHA)	1-to infinity
MFI framework (ZSM-5)	10-to infinity
Mordenite (MOR)	4–12

1.8. H₂S Selectivity

The ability of an adsorbent to selectively adsorb a component in a gas mixture is affected by the presence of many components in the mixture. Adsorbents may have the capability to adsorb multiple components at the same time [35,36]. As a result, the selectivity of adsorbents is an essential factor to consider while making your selection. In order to choose and evaluate zeolites that are capable of selectively adsorbing hydrogen sulfide from gas streams, it is vital to take into consideration the zeolites' capacity to absorb other contaminants, such as carbon dioxide and water. The polarity of zeolites depends on the Si/Al ratio [37] and is a significant factor in determining their selectivity. They are well attracted to zeolites due to the fact that methane and its homologues in natural gas are non-polar and polar molecules such as H_2S, CO_2, and water. As was said earlier, selecting the appropriate zeolite is essential to decrease the adsorption of CO_2 and H_2O molecules while simultaneously enhancing affinity toward H_2S molecules.

1.9. Adsorption Capacity

The number of contaminations that the adsorbent needs to remove is an essential factor in determining how successful the operation will be. A decrease in the length of the adsorption cycle results from an increase in the adsorption capacity, which improves the separation of the targeted molecule from the mixture. The adsorption capacity can be determined by calculating the ratio of the amount of the adsorbed molecule to the mass of the adsorbent, and is often expressed in the unit of mmol/g or mg/g.

The following equation can be used to determine the maximum adsorption capacity of a zeolite:

$$q_e = \frac{(C_0 - C_e)V}{m}$$

where, C_0 and C_e represent the initial and equilibrium concentration (ppm) of the H_2S, respectively; V (L) represents the total volume of gas mixture used in each experimental run; and m (g) represents the dry mass of the adsorbent that was used for the adsorption process. All concentrations are expressed in mg/g.

The adsorption capacity for continuous adsorption can be calculated from the breakthrough curves using the following equation [38]:

$$C_{ads} = \frac{Q_{tot} \cdot MW \cdot [C_{in} \cdot t_1 - (t_1 - t_0) \cdot 0.5]}{V_m \cdot m \cdot 10^3}$$

Q_{tot} = total gas flow rate (Nl/h).
MW = molecular weight of H_2S.
C_{in} = inlet H_2S concentration (ppmv).
t_1 = breakthrough time when the outlet concentration is 1 ppmv (h).
t_0 = breakthrough time at the last detection of 0 ppmv (h).

V_m = molar volume (24,414 Nl/mol). m = mass of adsorbent material (g).

2. Natural Zeolites

Although natural zeolites have adsorption properties that are several times higher than those of synthetic zeolites, very few natural zeolites have been studied in the context of the removal of hydrogen sulfide from a variety of gases.

A 94% hydrogen sulfide adsorption performance was reached by Pourzolfaghar et al. [39] from biogas using virgin zeolite without activation. This particular zeolite had a high Si/Al ratio of 5:99, which resulted in a higher adsorption capacity but was lower than the adsorption capacity of the modified zeolite. A number of experiments showed that virgin zeolite had natural regeneration.

The influence of CO_2 and moisture content on the removal of H_2S and SO_2 from biogas using naturally pure zeolite covered with TiO_2 utilizing ultrasonic-calcination investigated by Liu et al. [14]. Sintering for 2 h at 400 °C was found to be the best condition for obtaining maximum removal capacity and improved mechanical properties. To regenerate utilized TiO_2/zeolite, it was washed at 60 °C for 5 h, dried at 110 °C for 12 h, and then calcined at 400 °C for 2 h. As the amount of TiO_2 on zeolite increases, the formation of SO_2 rises. That is why 5% of TiO_2 onto zeolite demonstrated the best adsorption properties, with an adsorption capacity of 0.13 mmol/g (4.42 mg H_2S/g). As the competitive adsorption takes place in the presence of CO_2, H_2S adsorption capacity has decreased. It was found that moisture content decreased the adsorption capacity of the zeolite whereas adsorption capacity of TiO_2/zeolite increased due to TiO_2 photocatalysis.

Ahmad et al. [40] examined natural diatomite, which is a low-cost silica material, and tested its water and acid-treated modification in biogas purification. In order to prepare the treated diatomite, washing was done at a variety of temperatures, and sulfuric acid was applied in a variety of concentrations. Samples of diatomite that had been treated with water and those that had been treated with sulfuric acid were both dried in an oven at 105 °C for 24 hr. According to the findings, acid treatment made it easier to modify the surface area and functional group of the diatomite, which led to an increase in the adsorption capacity to 6.87 mg H_2S/g. On the other hand, water hydration reduced the contaminants and improved the diatomite pore volume, which led to an increase in the adsorption capacity to 3.82 mg H_2S/g. During the process of water purification, an increase in temperature results in a greater capacity for adsorption. It was discovered that a concentration of 5M H_2SO_4 produced the best results when purifying diatomite in order to acquire a high adsorption capacity.

Prasetyo and Soegijono Prasetyo and Soegijono [37] modified Bayah natural zeolites, which are high silica zeolites, in the ferric chloride hexahydrate solution using high-intensity ultrasonic waves. They then examined the H_2S adsorption performance of the modified Bayah natural zeolites. Minerals found in Bayah are primarily composed of clinoptilolite, with traces of mordenite that contain a variety of elements, including carbon, sodium, magnesium, potassium, calcium, and iron. Sonification was applied to a number of different time lapses. Based on the findings, it is possible to draw the conclusion that the time of sonification has no bearing on the distribution of particle sizes. The chemical modification of Bayah natural zeolite increased its adsorption ability by 70% to 117%.

In many situations, the zeolitic imidazolate framework ZIF-8 was used in CO_2 capture. Jameh et al. [41] investigated ZIF-8 synthesis and modification using methanol and toluene for CO_2 and H_2S removal from natural gas. The specific surface area and microporous pore volume of ZIF-8 increased as a result of methanol modification, demonstrating a high adsorption capability.

According to the abovementioned research, natural zeolites are also good at separating H_2S. Various procedures, including as high-temperature calcination, the addition of various metals, and acid processing, can be employed to improve their efficacy in H_2S removal. Table 4 highlights methods for removing H_2S using natural zeolites.

Table 4. Studies based on natural zeolites.

Zeolite Type	Selectivity/Adsorption Capacity	Reference
Virgin zeolite	94% adsorption performance	[39]
Pure zeolite covered with TiO_2	4.42 mg H_2S/g	[14]
Water treated diatomite	3.82 mg H_2S/g	[40]
Acid treated diatomite	6.87 mg H_2S/g	[40]
Bayah natural zeolite	70–117% adsorption performance	[42]

3. Synthetic Zeolites and Their Modifications

Because natural zeolites are insufficient for commercial use as catalysts and adsorbents, synthesized zeolites are utilized instead. It is necessary to improve the characteristics of zeolites. To that end, metals can be added, calcination temperatures can be changed, and the composition of zeolites can be altered in other ways. Metal ions are introduced into the zeolite structure by two methods: ion exchange and impregnation.

In order to remove hydrogen sulfide from the air at 100, 200, and 300 °C, Jafari et al. [43] examined Y and ZSM-5 (MFI), which are considered intermediate and high silica zeolites modified with 3% and 5% of magnetite nanoparticles. Drying and calcination were carried out at 105 °C for 10 h and 450 °C for 4 h, respectively, to purify and activate. After adding magnetite nanoparticles and calcining them, the modified zeolites' surface area, volume, and diameter decreased. On the other hand, the crystal structure was unaffected by either magnetite or calcination. Due to the presence of magnetite nanoparticles, zeolite Y's meso/micro-porosity increased when compared to ZSM-5. A weight ratio of 5% was determined to be the ideal loading percentage since a high loading percentage lengthens the breakthrough time. At an H_2S concentration of 120 ppm, a 5% -Y/Fe_3O_4 adsorbent was used to produce the greatest adsorption capacity, which was equal to 69.92 mg H_2S/g. This phenomenon can be explained through the chemisorption of H_2S by iron oxide.

Interesting research was carried out by Yokogawa et al. [37] to assess LTA (Zeolite A) and MFI (ZSM-5) zeolites and their Ag-doped samples to remove volatile sulfur compounds produced in a mouth. LTA and MFI zeolites were synthesized by the wet method and ion exchange of Ag was carried out and dried at 90 °C for 24 h. On both 0.02 g of Ag-doped LTA and MFI, the H_2S concentration was lowered to 24% in 2 h, to almost zero in 4 h, and to be almost zero H_2S concentration for 4 h and 8 h, respectively. In zeolites, experiments showed that adding alkali atoms enhances their capacity to recover hydrogen sulfide, and the Ag-doped LTA zeolite had a better capacity than the Ag-doped MFI. As peaks corresponding to Ag_2S were not identified in the XRD patterns, the authors described this phenomenon as the capture of H_2S by the zeolite pores. The addition of Ag to zeolites helps to increase the affinity toward H_2S.

At a range of temperatures (25–85 °C), Starke et al [34] studied the effect of increasing Ca^{2+} on the zeolite type of LTA, which is binder free and has a Si/Al ratio of 1. A breakthrough curve was evaluated in a fixed-bed adsorption unit and calcination was carried out before each experiment at 300 °C for 4h under a nitrogen atmosphere. The H_2S concentration was in the range of 50–2000 ppm. It was concluded that increasing the Ca^{2+} cations in the zeolite causes physisorption to dominate. Increasing the Ca^{2+} in the degree of exchange rises the adsorption capacity due to higher ionic charge of Ca^{2+}; this because it causes strong interactions to form between the Ca and H_2S molecules. Temperature has a negative effect on the adsorption capacity.

Nguyen and his team [44] synthesized Faujasite zeolite hydrothermally and ion-exchanged with divalent metal ions (Co^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Ca^{2+}, and Zn^{2+}). H_2S adsorption was carried out in continuous fixed bed. Ion-exchange modification of NaX with Co, Cu, and Zn considerably enhanced the adsorption capacity. It can be explained by the reaction between the CoO, CuO, and H_2S molecules. When compared to raw X zeolite, the CoX, CuX, and ZnX zeolites showed more than 7, 13, and 24 times the H_2S adsorption capability, respectively, which means the ZnX sample had a higher adsorption capacity of 23.5 mg H_2S /g.

Many researchers are attempting to remove H_2S with the help of the Ag ion. Kumar et al. [10] examined Ag and Cu modified X and Y zeolites to separate H_2S from gas streams containing He, N_2, CO_2, CO, and H_2O at room temperature and 150 °C. X and Y zeolites had an Al/Si ratio of 1.3 and 2.4. CuX and CuY samples showed high adsorption capacity due to forming new active sites at 150 °C whereas the adsorption capacity of the NaX, AgY, and AgX samples declined. Despite the presence of the various gases in the mixture, AgX and AgY zeolites were able to remove H_2S. However, CuX and CuY were unsuccessful to remove H_2S in the presence of 2% CO. It is possible that the impregnation of copper to zeolite increased CO's affinity to the adsorbent while Ag attracted H_2S.

Chen et al. [45] tested an ion-exchanged NaX zeolite with Zn, Co, and Ag to identify the adsorption performance of H_2S and COS from Claus tail gas. CoX, ZnX, and AgX ion-exchanged zeolites were synthesized using their nitrate solution and dried at 100 °C. Characterization of the samples was done by SEM (see Figure 3), XRD, and FTIR techniques to prove the ion exchanging of the metals. A dynamic adsorption experiment was carried out in a fixed bad adsorption column at 25 °C. Although the BET surface area of the ion-exchanged AgX zeolite decreased to 30% compared to NaX, AgX had the largest H_2S and COS breakthrough capacity, with 1.53 mmol/g (52.02 mg H_2S/g) and 10.5 μmol/g (0.63 mg COS/g), respectively. This can be explained by the chemical adsorption between the AgX zeolite and H_2S.

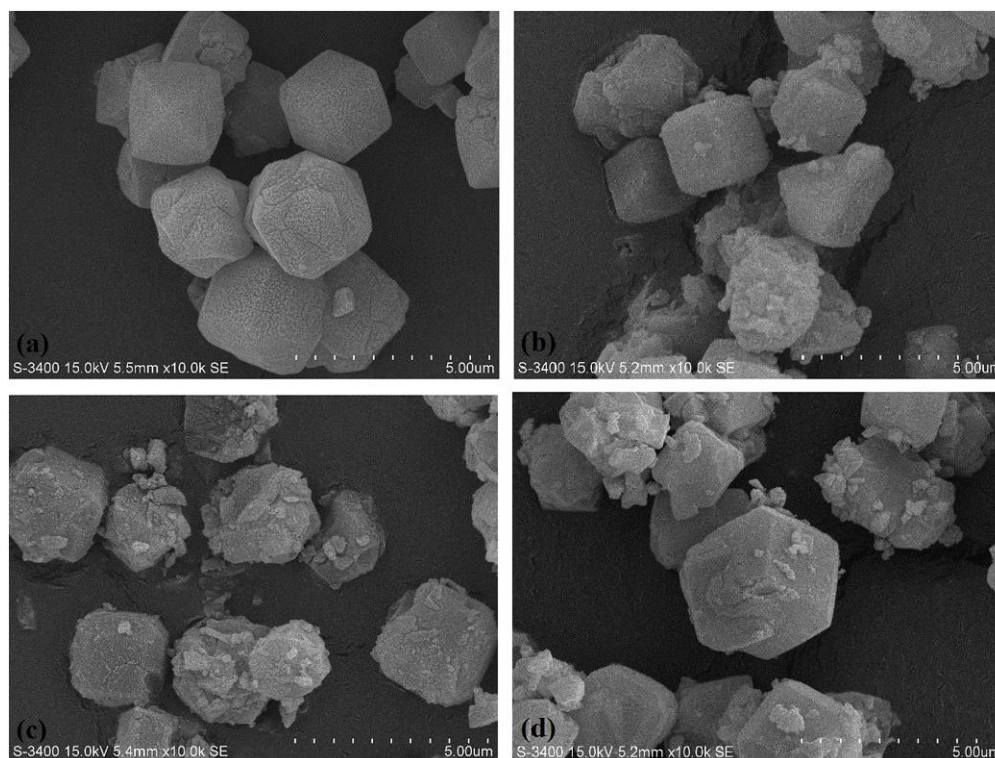**Figure 3.** SEM images of NaX (**a**), CoX (**b**), ZnX (**c**), and AgX (**d**), reprinted from [45], with permission of Elsevier.

Nevertheless, regeneration of the AgX zeolite under various conditions was investigated. Regeneration in the presence of air at 350 °C was better, and the AgX sample exhibited a remarkable thermal stability, retaining its original structure even after six adsorption–regeneration cycles.

The performance of the Cu-modified 13X was investigated by Barelli and colleagues [13] in the separation of H_2S from biogas. Experiments were carried out under a broad spectrum of operational conditions (temperatures ranging from 30 °C to 120 °C, and H_2S concentrations ranging from 200 to 1000 ppm) in order to determine the optimal operating parameters. Temperature has a beneficial effect on performance, as demonstrated by the

fact that a higher adsorption capacity of 13X Ex-Cu zeolite was obtained (40 mg H_2S/g) when the temperature was set to 120 °C. When the matrix composition was changed, the adsorption capacity decreased because competitive adsorption took place. The 13X Ex-Cu zeolite had an adsorption capacity of 14mg H_2S/g and 23 mg H_2S/g with the pure CO_2 and CH_4, respectively, due to the increase in Cu^{2+} that causes π-complexation between the Cu^{2+} ions and sulfur compounds.

Simultaneous removal of H_2S and SO_2 from the Claus tail gas using the 13X zeolite was carried out by Yang et al. [46]. The adsorption was performed in a simulated Claus gas containing 20,000 ppmv H_2S, 10,000 ppmv SO_2, 15 vol% water vapor, and the balance N_2 gas at 150 °C. According to the breakthrough curve, the fresh 13X zeolite showed an adsorption sulfur capacity of 179.7 mg S/g for H_2S and SO_2. Regeneration was done by purging of N_2 at 490 °C for 120 min with the space velocity of 1000 h^{-1}. The adsorption sulfur capacity decreased to 148.1 mg S/g after five adsorption–regeneration cycles due to formation of sulfate in the pores of 13X, which causes the blockage of pores.

Modifying the 13X zeolite with Ag and Cu by impregnation, to remove the organic sulfur compounds from natural gas, was investigated by Zhu et al. [47]. Modification of 13X with Ag increased the adsorption capacity by 1.6 times (64.8 mg S/g) compared to the raw 13X. Calcination at high temperatures improved the performance of the modified zeolite, with 450 °C being the best one. Cu/13X also showed a high adsorption capacity in the following sequence: ethyl mercaptan > methyl sulfide > dimethyl disulfide. The results show that modification of the 13X zeolite with metals such as Ag and Cu increases their adsorption affinity to organic sulfur compounds. The authors assumed that Cu/13X- and Ag/13X-modified zeolites show higher efficiency in H_2S separation. Adding metal ions to zeolite increases the adsorption capacity due to a Metal-S bond.

Bareschino et al. [48] recently conducted studies to determine the saturation of NaX zeolite with H_2S. The effects of H_2S concentration, temperature, and adsorbent age were investigated, and it was discovered that the adsorbent does not fully saturate since H_2S oxidation occurs:

$$H_2S + 1.5O_2 = SO_2 + H_2O$$

$$H_2S + 0.5O_2 = S + H_2O$$
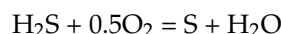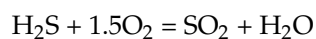
At high temperatures, elemental S is formed in the pores of zeolite; thus, no zero H_2S concentration can be achieved by regenerating the adsorbent.

Recent research conducted by Kulawong et al. [9] examined the effectiveness of the Ag-exchanged NaX zeolite in removing H_2S from an anaerobic digestion reactor. The preparation of this zeolite required varying concentrations of $AgNO_3$ (11.5%, 34.1%, 71.6%, 76.7%, and 78.8%) in order to get varying degrees of silver loading on the zeolite by heating it at 40 °C for 2–12 h. As the amount of silver loaded into the system rose, the H_2S concentration dropped, demonstrating that silver makes H_2S more attractive. As a result, an increase in the quantity of Ag loaded was accompanied by an increase in the effectiveness of H_2S removal. Since the maximum content was not statistically significant, the NaX zeolite with a lower Ag concentration of 34.1 wt% labeled as AgX2 would be more cost-effective with an adsorption performance of 97.35%. This is because the maximum content did not meet the criteria for statistical significance.

Manullang et al. [49] investigated the influence of the Zn/Zeolite ratio and calcination temperature on the separation of hydrogen sulfide from biogas. The impregnation method was used to prepare the samples at concentrations of 10, 20, and 30 wt/v% ZnO. Prepared samples were activated for 3 h by calcination at 200, 300, and 400 °C. The crystal structure of zeolites can be damaged and the surface of a zeolite covered by metal due to the sintering of metal salts at high temperatures, resulting in a loss in adsorption performance. The optimal parameters for separating H_2S from biogas were found: a Zn/Zeolite ratio of 20% and a calcination temperature of 300 °C. Adsorption capacity reached up to 6.36 mg H_2S/g adsorbent under these conditions, and the purification rate was 99%.

In order to evaluate the effect of silver on NaA zeolite for the removal of hydrogen sulfide, Bahraminia et al. [50] studied synthesized NaA nano zeolite and its Ag-exchanged sample. NaA zeolite was synthesized hydrothermally and AgNaA was prepared by ion-exchange and both dried at 60 °C for 12 h. The structure of the samples was confirmed by XRD and SEM techniques. The adsorption capacity of the NaA zeolite with Ag^+ ions was found to have increased (33.24 mg H_2S/g). In addition, the regeneration of AgNaA was carried out five times at a temperature of 350 °C. As a result of the development of sulfur on the surface of the zeolite, the adsorption capacity showed a modest decrease of 5%.

The equilibrium and dynamic behaviors of natural gas separation, using Na-SSZ-13 zeolite, were studied by Thomson [51]. The adsorption process was carried out in a dynamic column breakthrough (DCB) apparatus. A feed gas mixture of CH_4, C_2H_6, CO_2, and H_2S at different concentrations was used. Binary, ternary, and quaternary DCB experiments were carried out to assess the adsorption performance of Na-SSZ-13. COS formation has occurred because of the presence of CO_2 and H_2S in the feed gas. Ideal Adsorption Solution Theory (IAST) is applied to obtain the mixture adsorption data. When the IAST was used to simulate the gas adsorption mixtures on the Na-SSZ-13 zeolite, the adsorption behavior and experimental breakthrough curves matched well.

The effects of temperature, H_2S inlet concentration, gas matrix, and adsorption/desorption cycles of the adsorption of H_2S on the industrial molecular sieves (IMS) were studied by Georgiadis et al. [52] theoretically and practically. The LTA-type zeolite structure framework was proved by characterization of IMS, which had a BET surface area of 590 m^2 g^{-1}. Adsorption was done at 35, 50, and 100 °C, and reduction in the adsorption capacity occurred as physical adsorption took place, which is exothermic. IMS had the highest adsorption capacity of 122.8 mg H_2S/g at 35 °C. Studies at different concentrations of H_2S have shown that the higher the concentration, the higher the adsorption capacity. The adsorption capacity was reduced due to the presence of CO_2 in the gas composition and its competitive adsorption with H_2S. Although adsorption/desorption cycles were carried out 15 times, no significant changes were observed on the H_2S uptake.

At room temperature, Rezaei et al. [53] compared the ETS-2 adsorbent exchanged with Ag, Ca, Cu, and Zn metals to a commercially available adsorbent, R3-11G. In comparison to R3-11G, the metal-exchanged ETS-2 zeolite showed better effective adsorption properties. The Cu-exchanged ETS-2 zeolite had the highest H_2S capacity as an absorbent, 29.7 mg H_2S/g.

For the sake of safety, H_2S was removed from the simulated gases containing nitrogen and other inert gases in many studies. Heck et al. [54] conducted pressure swing adsorption of concentrated H_2S (0.1–0.7%) and CO_2 from a feed gas containing CH_4, CO_2, and H_2S, which is similar to natural gas using commercially available zeolites, namely, 4A, 5A, and 13X. The effect of the concentration of H_2S and pressure were studied by a number of experiments. 13X and 5A zeolites may remove H_2S to a nearly zero concentration. A 100% recovery of H_2S was achieved by desorption in 13X and 4A. It was concluded that the PSA method can be used industrially for the removal of H_2S from natural gas.

Bowen et al. [55] investigated hydrogen sulfide removal from natural gas using titanosilicite zeolite (TS-1) in the presence of hydrogen peroxide and examined the effect of reaction temperature and H_2O_2 concentration on the catalytic oxidation. The result showed that increasing the reaction temperature and H_2O_2 concentration increase the catalytic oxidation of TS-1 towards H_2S. In Table 5, studies based on modification of synthetic zeolites are summarized.

Table 5. Studies based on modification of synthetic zeolites.

Zeolite Type	Selectivity/Adsorption Capacity	Modification Type	Reference
5% -Y/Fe_3O_4	69.92 mg H_2S/g.	Impregnation	[43]
Ag doped LTA	0% H_2S concentration after 4 h	Wet method and impregnation	[37]
Ag doped MFI	0% H_2S concentration after 8 h	Wet method and impregnation	[37]
LTA modified by Ca	An increase in physical adsorption	Ion-exchange	[34]
ZnX	23.5 mg H_2S/g	Ion-exchange	[44]
AgX	61.2 mg H_2S/g	Ion-exchange	[10]
AgY	44.8 mg H_2S/g	Ion-exchange	[10]
AgX	52.02 mg H_2S/g	Ion-exchange	[45]
13X Ex-Cu	40 mg H_2S/g with N_2	Ion-exchange	[13]
13X Ex-Cu	14 mg H_2S/g with pure CO_2	Ion-exchange	[13]
13X Ex-Cu	23 mg H_2S/g with pure CH_4	Ion-exchange	[13]
13X	179.7 mg S/g		[46]
AgX	64.8 mg S/g	Impregnation	[47]
Ag exchanged NaX	97.35% adsorption performance	Ion-exchange	[9]
20% ratio of Zn/Zeolite	6.36 mg H_2S/g	Impregnation	[49]
AgNaA	33.24 mg H_2S/g	Ion-exchange	[50]
Industrial molecular sieves (IMS)	122.8 mg H_2S/g		[52]
Cu exchanged ETS-2	29.7 mg H_2S/g	Ion-exchange	[53]
H_2O_2/titanosilicite	An increase in catalytic oxidation		[55]

4. Zeolite-Based Adsorbents Synthesized from Various Sources

In recent years, zeolite-based adsorbents used in the separation of H_2S from gas mixtures have been synthesized from various cheap raw materials because they are widely available and have a low production cost.

Jalil R. Ugal et al. [56] studied the adsorption capacity values of 3A, 4A, and 5A zeolites prepared from Iraqi kaolin by the ion-exchange method. Characterization results of the prepared samples proved that 3A, 4A, and 5A molecular sieves were successfully synthesized and they had a similar structure as the standard type. 4A has a high affinity for H_2S according to the values of the Langmuir isotherm, which best describes the gas–solid face adsorption. 5A zeolite showed an adsorption capacity of 79.384 μmol/g (2.7 mg H_2S/g). The H_2S adsorption capacity increased with a decrease in temperature from 55 °C to −5 °C. This is explained by the authors in that a rise in temperature weakens the adsorption interactions between the adsorbent and the adsorbate. This indicates that the synthesized molecular sieves on the basis of kaolin are suitable to use in the H_2S separation.

Liu et al. [57] carried out hydrogen sulfide removal using 4A zeolite synthesized from naturally abandoned zeolite, namely, attapulgite (ATP). 4A zeolite was synthesized under various ratios. The effects of the ratio of silicon to aluminum, ratio of sodium to silicon, ratio of water to sodium, crystallization temperature, and time were investigated in the removal of H_2S. From the breakthrough curves of experiments under various conditions and ratios (see Figure 4), it can be seen that there is competitive adsorption between H_2S and N_2 at the beginning. The ratio of silicon to aluminum has a substantial influence on the performance of H_2S removal, as demonstrated in the figures; however, the ratio of sodium to silicon has a weak impact on the performance of H_2S removal. When considering both factors, a ratio of 1.5 might be the best possible figure. A low ratio of water to sodium was ideal since ATP naturally contains elements such as magnesium, calcium, and iron. These elements can form their oxides, which have a favorable impact on the removal of H_2S. From these findings, it can be concluded that the zeolite 4A synthesized under the following conditions: n (SiO_2)/n (Al_2O_3)) = 1.5, n (Na_2O)/n (SiO_2) = 1.5, crystallization at 90 °C for 4 h, n (H_2O)/n (Na_2O) = 30) showed a high adsorption capacity of 8.36 mg H_2S/g sorbent and a saturation sulfur sorption capacity (that is complete adsorption capacity that can no longer adsorb H_2S) of 12.4 mg H_2S/g at 50 °C. Because of its distinguished properties, 4A zeolite synthesized from attapulgite is proposed as a promising material for H_2S adsorption. Furthermore, the 4A was regenerated at 350 °C for 2 h using nitrogen

purging at a flow rate of 200 mL/min. Characterization analyses showed no significant changes in BET surface area, crystal structure, and surface group after regeneration.
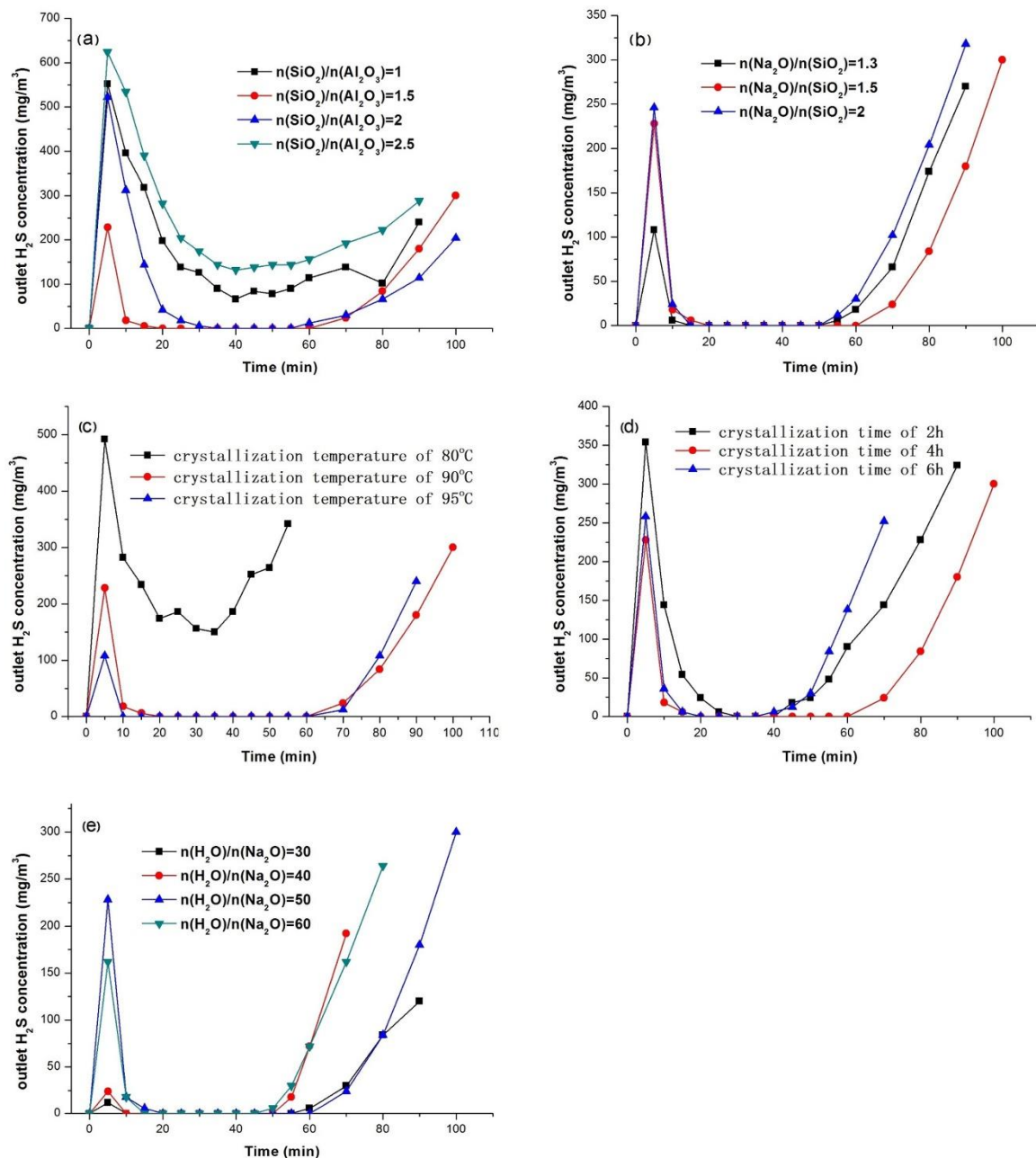

Figure 4. H$_2$S adsorption breakthrough curves at 25 °C under different synthesis conditions: (**a**) at various (SiO$_2$)/n (Al$_2$O$_3$) ratios (**b**) at various (Na$_2$O)/n (SiO$_2$) ratios, (**c**) at various temperatures, (**d**) at various crystallization time, (**e**) at various (H$_2$O)/n (Na$_2$O) ratios, reprinted from [57], with permission of Elsevier.

Oliveira et al. [58] examined H$_2$S adsorption on NaY zeolite in equilibrium and fixed bed conditions. NaY zeolite was prepared using kaolin clay and examined its adsorption properties for the H$_2$S removal from natural gas in continuous PSA. The Si/Al ratio of NaY was 2.8. Adsorption isotherms obtained at temperatures of 20, 30, and 40 degrees Celsius, up to a partial pressure of 1.2 bars of hydrogen sulfide, are advantageous and offer maximum adsorption capacities that are greater than 6.0 mol kg^{-1} (204 mgH$_2$S/g).

Abdullah et al. [59] studied the influence of ZnO on Na-A zeolite synthesized by impregnation from Malaysian kaolin in biogas desulfurization. ZnO was employed to

increase the adsorption capacity of zeolite and because its low cost compared to other oxides. When the loading rate was increased from 10 to 20 wt%, both the micropore area and the micropore volume decreased. However, there was no substantial change found even after increasing the loading rate from 20 to 30 wt%, which indicates that the loading rate was exceeded. It was noticed that the highest adsorption capacity of 15.75 mg S/g sorbent H_2S when 20 wt% ZnO was loaded onto Na-A. The fact that the characteristics of the used adsorbent were not recovered as a result of regeneration at temperatures of 100 and 200 °C is evidence that chemical adsorption took place by the following equation:

$$ZnO + H_2S(g) = ZnS + H_2O$$
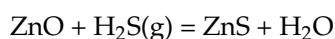
As a low-cost material, a water–glass solution was used as an Si source and a 13X molecular sieve was synthesized hydrothermally to reduce H_2S from propane by [12]. The BET surface area of the synthesized 13X sample had 462.56 m^2/g. The adsorption process was done at room temperature and different pressures up to 25 bar. The adsorption capacity of the synthesized 13X zeolite was obtained at 10 bars and no considerable influence on the adsorption capacity was observed after increasing the pressure. Table 6 summarizes the approaches of H_2S removal using synthetic zeolites.

Table 6. Studies on synthetic zeolitic adsorbents from various sources.

Zeolite Type	Source	Selectivity/Adsorption Capacity	Synthesis Method	Reference
5A	Iraqi Kaolin	2.7 mg H_2S/g	Ion-exchange	[60]
4A	Attapulgite	8.36 mg H_2S/g	Hydrothermal	[57]
NaY	Kaolin clay	5.345 mg H_2S/g	Hydrothermal	[58]
20 wt% ZnO/Na-A	Malaysian kaolin	15.75 mg S/g	Impregnation	[59]
13X	Water-glass solution	44 mg H_2S/g (20ppm)	Hydrothermal	[12]

5. Newly Developed Adsorbents from Wastes

One of the most important things that contributes to successful and feasible development is the utilization of inexpensive raw materials on an industrial scale. As a result, a number of research initiatives have been abandoned on the development of novel compounds derived from less expensive and obsolete basic materials. The production of zeolites requires the utilization of a number of different minerals, including kaolinite, fly ash, sludge, asbestos, and rice husk. The investigation of wastes as an adsorbent in the separation of H_2S would open up a new sector.

Cebula et al. [61] synthesized a universal adsorbent, namely, Halloyfill, from a halloysite mineral—which is an aluminosilicate clay mineral belonging to the kaolin group— and applied it to the removal of various pollutants such as siloxanes, H_2S, and NH_3 generated from biotechnological processes. The results showed that it can remove NH_3 (95–99%), H_2S (above 99%-21.3 mg H_2S/g), and volatile organic compounds (70–81%). The authors also proposed that the spent adsorbent can be used as a fertilizer in agriculture and gardening.

$CaCO_3$ was the primary component of two kinds of the waste solids that Awe and colleagues [62] investigated as potential H_2S adsorbents. Fresh calcite and commercially activated carbon (AC) were utilized as comparative materials in order to validate the adsorption performance of the synthesized adsorbent. In addition, AC-$CaCO_3$ waste mixtures with a variety of different ratios were researched. In 540 min, 15 mg H_2S was adsorbed when the weight ratio of AC to $CaCO_3$ was 3:1, whereas AC only absorbed 14 mg H_2S over that same time period. It is possible to explain the presence of a variety of metals in the solid waste, including Ca, Mg, and Fe. The findings demonstrated that using wastes containing $CaCO_3$ as an adsorbent for H_2S removal was more effective than using activated carbon or calcite, which are both available for purchase in the marketplace.

Three waste-derived adsorbent materials (wood-derived biochar (WDB), sludge-derived activated carbon (SDC), and activated ash) were studied by Zhu et al. [63] for the separation of H_2S from simulated biogas (CH_4-to-CO_2 ratio at 1.5 and H_2S concentration at 200 ppm). WDB and activated ash were activated at 700 °C, while SDC was activated at 600 °C. Characterizations of the pre-treated adsorbent were analyzed by TGA, XRF, SEM, and BET. The outlet concentration of H_2S was measured using a mass spectrometer to determine the adsorption capacity. Activated ash showed the highest adsorption capacity, at 3.22 mg H_2S/g, among the materials; this was because chemisorption occurred as a result of the presence of alkaline mineral species such Fe, Cu, and Mn, which have a tendency to react with H_2S. Wood-derived biochar has an adsorption capability of 2.2 mg H_2S/g due to its high surface area of 210.18 m^2/g. To demonstrate the existence of physical adsorption, the surface area of WDB decreased from 210.18 $m^2\ g^{-1}$ to 96.95 $m^2\ g^{-1}$. This occurred because high porosity was responsible for capturing the H_2S molecules. Physical adsorption was proved by reducing the surface area of WDB, as the H_2S molecules are captured by the high porosity.

Asaoka et al. [64] synthesized an H_2S adsorbent by combining coal fly ash and blast furnace cement. In the optimal conditions, adsorption capacities of 650 g-H_2Sm^{-3} (62.15 mg H_2S/g, calculated according to the density of average coal fly ash [65] and blast furnace cement [66]) under dry conditions and 730 g-H_2Sm^{-3} (71,71 mg H_2S/g) under humid conditions were achieved with a component ratio of 87:13 and a calcination temperature of 700°C. The synthesized adsorbent can remove both dry and humid H_2S up to 99.1%, as H_2S oxidation into sulfate, meaning chemisorption occurred.

Coal fly ash and blast furnace cement were used in the synthesis of H_2S adsorbent by Asaoka et al. [64]. With a component ratio of 87:13 and a calcination temperature of 700°C, it was possible to achieve adsorption capacities of 650 g-H_2Sm^{-3} (62.15 mg H_2S/g, calculated according to the density of average coal fly ash [65] and blast furnace cement [66]) under dry conditions and 730 g-H_2Sm^{-3} (71,71 mg H_2S/g) under humid conditions. These results were achieved as a result of H_2S oxidation to sulfate, which is chemisorption. The adsorbent is capable of removing up to 99.1 % of H_2S in both dry and humid conditions.

Mbugua et al. [67] investigated the use of zeolitic rock from the Eburru deposit as well as other materials (maize cobs, steel wire, desulphurizer, and worn-out tyres) for the purpose of upgrading of biogas by removing CO_2 and H_2S. As a result of the polarity of CO_2, zeolite rock demonstrated excellent performance; in contrast, desulfurizer was able to remove H_2S at a rate of 97.78%. The presence of metals such as manganese, magnesium, iron, and zinc in zeolitic rock can be regarded as having certain characteristics.

Although iron has a tendency to chemically react with H_2S, Salimi et al. [68] studied the modification of adsorbents, namely, bentonite and sludge, with iron and copper to remove H_2S and mercaptans from a refinery outlet gas. Depositions of Fe and Cu metals onto bentonite and sludge were proved by SEM–EDS analysis. The authors also explored the effect of the flow rate on the adsorption performance, concluding that a low flow rate is preferred. Regeneration of the adsorbent was done using gas and steam at 200 °C after three time cycles, with an adsorption capacity reduction observed. Iron-modified bentonite demonstrated a high adsorption capacity for H_2S (32.256 mg H_2S/g) and mercaptan (0.98 mg/g), whereas the copper-modified sludge had an adsorption capacity for H_2S (11.18 mg H_2S/g) and mercaptan (0.81 mg/g).

Gasquet et al. [69] has recently attempted to examine and improve the H_2S adsorption properties of sewage sludge-derived ash (SSA) and its modification with sand and activated carbon. Modification of SSA with 20% activated carbon showed an increase in the adsorption capacity of up to 186 mg H_2S/g. Since elemental sulfur was observed by characterization techniques, the authors explained this by chemical adsorption due to reactional sites between HS- and oxygen that were created by the microporosity of the activated carbon.

Various materials, such as sand (S) silica blue (SB), iron-exchanged sand (IES), zeolite 13X (Z), iron-exchanged zeolites (IEZ), and the waste material acid mine drainage sludge

(AMDS), were investigated as H_2S adsorbents in previous research [70]. Experiments were done using a gaseous mixture containing 100–1000 ppmv of H_2S in N_2 in a pilot lab setup at 25 °C. Characterization of adsorbents were analyzed before and after adsorption. AMDS showed a high H_2S adsorption capacity of 312.73 g H_2S/g compared to other adsorbents at a flow rate of 0.5 L/min, when the initial concentration of H_2S was 1000 ppmv. However, as the flow rate increased, the H_2S adsorption capacity decreased.

The majority of waste-based adsorbents are composed of metals such as Fe, Cu, and Mg, all of which have a tendency toward chemisorption. Studies on the waste-based adsorbents were summarized in Table 7.

Table 7. Studies on the waste-based adsorbents.

Adsorbent Type	Selectivity/Adsorption Capacity	Reference
Halloyfill (halloysite based adsorbent)	above 99% H_2S removal (21.3 mg H_2S/g)	[61]
$CaCO_3$-containing wastes	outperforms commercially activated carbon	[62]
Activated ash	3.22 mg H_2S/g	[63]
Wood-derived-biochar	2.2 mg H_2S/g	[63]
Coal fly ash and blast furnace cement	62.15 mg H_2S/g (650 g-H_2S m^{-3}) under dry conditions	[64]
Coal fly ash and blast furnace cement	71.71 mg H_2S/g (730 g-H_2S m^{-3}) under humid condition	[64]
Zeolite rock	97.78% performance	[67]
Iron-modified bentonite	32.256 mg H_2S/g	[68]
Copper-modified sludge	11.18 mg H_2S/g	[68]
AC modified sewage sludge derived ash	186 mg H_2S/g.	[69]
Acid mine drainage sludge (AMDS)	312.73 g H_2S/g	[70]

6. Conclusions

In the separation of H_2S gas from gas mixtures, the presence of other gases in the mixture, such as CO_2, H_2O, and CO, complicates the process because of competitive adsorption. Therefore, it is very important to find and synthesize efficient zeolites with a high adsorption capacity, selectivity, and regenerability that can separate H_2S under a variety of conditions. Natural and synthetic zeolites, and their modifications, are widely used in the separation of H_2S from various gaseous mixtures. It is difficult to find the most effective adsorbent because there are so many different structural types of zeolites, modification possibilities, and conditions to consider when removing H_2S. However, by understanding the properties of zeolites and the gas to be removed, the proposed zeolite or its modification can be assumed for the screening in the separation processes. Linde Type A (4A and 5A) and Faujasite (13X) zeolites with a low silica content, and their modifications with Cu and Ag, which have good adsorption properties, are very good candidates in this case.

The adsorption of hydrogen sulfide by zeolites is considered to be physical adsorption in most cases. The modification of zeolites can increase their attraction to H_2S, and this can sometimes lead to the development of chemical adsorption. To date, many research attempts have explored the adsorption of H_2S by modified zeolites using ion-exchange and impregnation methods, and very promising results are being obtained and their application is being proposed on an industrial scale. In recent studies, a NaX zeolite modified with a Ag^+ cation has been suggested as a highly effective adsorbent in H_2S removal.

Moreover, adsorbents made from wastes, such as activated ash, bentonite, sewage sludge, and acid mine drainage sludge, have been proposed as effective H_2S adsorbents. The adsorption capacity of AC-modified sewage sludge toward H_2S is high, but their regenerative ability has not been investigated. Although a very high adsorption capacity of 312.73 g H_2S/g of acid mine drainage sludge (AMDS) has been identified by Ahn et al. [70], this is somewhat far from the expectation. Because an adsorbent with such an adsorption capacity is not known to us, we have requested that the author [71] verify these statistics.

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