A review on H₂S adsorption by metal-organic frameworks for air purification application

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ABSTRACT

Removing hydrogen sulfide (H₂S) from the air stream in the workplace is important because this toxic gas can cause health problems for workers and destructive effects on equipment. Metal-organic frameworks (MOFs) are one of the most suitable materials for H₂S removal and separation. This review study attempted to comprehensively collect the studies and research regarding the removal of H₂S from the air stream using MOFs as an effective adsorbent. The databases of Google Scholar, Pub-Med, Scopus, and Web of Science were used in this study. All sections of the articles were reviewed to extract the required data. Keywords such as hydrogen sulfide, metal-organic frameworks, air purification, removal, and adsorption were used to extract the relevant articles. The results showed that UIO-66 and TOUO were the most commonly used MOFs for H₂S absorption. The average H₂S absorption among all MOFs was 14.92 mg/g. Advances in MOF design, stability, regeneration efficiency, and process integration further enhance their performance, making them more attractive for industrial-scale applications in gas purification and other separation processes. This review article could provide useful information and insight into the remarkable progress in the field of H₂S adsorption by MOFs.

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1. Introduction

Over the past few years, there has been a growing concern about the emission and release of toxic pollutants and harmful gases from diverse sources into the atmosphere [1]. Controlling and restricting the emission of these pollutants poses a significant global challenge, as these compounds have detrimental and destructive impacts on both human health and the environment [2]. These compounds include chemicals and various groups such as volatile organic compounds (VOCs), particulate matter (PM_{10} and $PM_{2.5}$), NO_X, SO_X, H_2S, CO, CO_2, NH_3, etc. [1-4]. Among these pollutants, toxic or chemical asphyxiant compounds such as H_2S are recognized as particularly serious and significant [2, 5]. Chemical asphyxiants interfere with oxygen transport by inhibiting the electron transport chain system in mitochondria, eventually leading to tissue hypoxia so that delivery, usage, and consumption of oxygen in the human body are cut off [5]. Exposure to asphyxiants in occupational and environmental areas is abundant [6].

In order to protect both humans and the environment, extensive efforts have been dedicated to capturing and eliminating harmful gases, such as chemical asphyxiants [7-12]. Chemical absorption is considered one of the effective methods for capturing harmful gases. However, this technique has some drawbacks, including the substantial energy consumption required to regenerate used absorbent solutions and the loss of solvent caused by evaporation [13, 14]. Recently, researchers have shown increasing interest in the physical adsorption technique, which can potentially overcome the limitations associated with chemical absorption methods [14]. The physical adsorption method uses solid adsorbents, including porous carbon maters [15, 16], zeolites [17, 18], and MOFs [19-21] [14, 20]. In recent studies regarding capturing toxic gases, MOFs are the most suitable candidates for separation [22].

MOFs are a rising class of porous crystalline materials that combine the benefits of organic and inorganic components. They consist of metal ions or clusters intricately linked with organic linkers, creating a hybrid structure with exceptional properties [23]. MOFs exhibit immense potential for various applications, such as gas storage and separation [24-26], the capture and adsorption of harmful gases [27-30], and the degradation of chemical warfare agents [31-34], thanks to their significant surface areas, tailorable pore sizes, versatile functionalities, and excellent thermal and chemical stability.

In recent years, there has been a significant surge in the synthesis and investigation of numerous MOFs for gas adsorption. MOFs encompass the following essential elements that play a pivotal role in capturing and adsorbing gases:

I. Versatile functionalization: MOFs can be functionalized with various components to exhibit selective adsorption towards specific harmful gases. For example, incorporating specific functional groups or metal clusters into MOFs can enhance their affinity for certain harmful gases, leading to improved adsorption performance. This functionalization can be tailored to target specific pollutants of interest [35-38].

II. Regeneration and reusability: MOFs can be regenerated, allowing for their reuse in capturing harmful gases. The captured gases can be desorbed by subjecting the MOFs to appropriate conditions, such as temperature or pressure changes, effectively restoring the MOFs' adsorption capacity. This renewability enhances the cost-effectiveness and sustainability of MOFs for gas capture applications [39-41].

III. Catalytic degradation: Some MOFs can be functionalized with catalytic sites that facilitate the degradation or transformation of harmful gases into less toxic or benign forms. These catalytic MOFs can promote chemical reactions that convert the captured gases into less hazardous compounds, mitigating their environmental impact [42].

The key factors enhancing hydrogen sulfide retention include surface chemistry, porosity, and the presence of inorganic matters, which make the MOFs the best choice to capture the H_2S [43].

In addition to the benefits of MOFs, the challenges associated with the use of MOF technology include:

a) Stability: Some MOFs can be prone to structural collapse or decomposition in the presence of gases or under certain conditions, thereby limiting their long-term stability.

b) Cost: The synthesis and production of MOFs can be relatively expensive compared to traditional

adsorbents, which may affect their commercial viability on a large scale.

c) Regenerability: The MOF should be capable of efficiently desorbing H_2S, allowing for multiple cycles of adsorption and desorption without a significant loss of performance [44].

Based on the study searches, it appears that the last review studies on H_2S were conducted before 2019; therefore, the most recent studies before this date were chosen with a stricter screening on the selection of articles. Along with the introduction of different methods of MOFs synthesis, a new method called ionic liquids has also been mentioned in this manuscript; it has attracted the attention of researchers due to its high selectivity. In the table of studies, most of the laboratory parameters that are important in eliminating H_2S have been expressed. In previous studies, however, this issue has not been fully mentioned. This paper presents a comprehensive review to highlight the factors and issues associated with the use of various MOFs for the adsorption and capture of H_2S.

2. Toxic Asphyxiants

Many widely used gases pose an asphyxiation hazard. Asphyxiants are gases that act as poisonous substances, resulting in respiratory distress and ultimately leading to asphyxia. It is achieved by displacing oxygen in the air [7]. Taking only one or two breaths in an oxygen deficient atmosphere may cause serious and prompt effects, including unconsciousness [6]. There are two types of asphyxiation hazards, namely simple asphyxiants and chemical asphyxiants; both affect the supply of oxygen in the air and have the same health consequences and impact [45].

A simple asphyxiant refers to a gas that does not cause additional health effects and is not considered a "poison" in the traditional sense. Simple asphyxiants are of particular concern in enclosed spaces. When these gases displace oxygen in higher concentrations, they make the atmosphere hazardous for humans [6]. They are often odorless and lack toxicity. Examples of gases with an asphyxiant hazard include hydrogen, carbon dioxide, Freon, methane, and nitrogen. In contrast, exposure to chemical asphyxiants directly impairs the transport of oxygen via

hemoglobin or interferes with the efficient use of oxygen at the tissue level via inhibition of oxidative phosphorylation [45]. They are commonly colorless and odorless gases. Chemical asphyxiants are highly toxic and can prove fatal if inhaled. Even a single exposure to a high concentration of these gases can lead to long-lasting effects, such as the development of asthma. H_2S is an example of a chemical asphyxiant. H_2S is generated as a by-product in various industrial processes and settings, including sewage treatment plants, the petroleum industry (oil and gas wells, refineries, and pipelines), mining and tunnels within mineral rock formations, and the pulp and paper industry during the breakdown of wood into pulp [2]. H_2S is also produced in sulfur springs, caves, and other underground natural gas fields. It is often present in compost pits and sewers [46].

H_2S is a colorless gas that has a distinct smell resembling rotten eggs. It is highly toxic, corrosive, and flammable. Due to its density, H_2S tends to accumulate in low-lying and poorly ventilated areas. Exposure to H_2S can irritate the eyes and mucous membranes. One notable effect of H_2S exposure is knockdown, which can occur immediately after exposure to high concentrations [47]. H_2S causes eye, nose, and throat irritation at concentrations as low as 5 ppm and is fatal over 1000 ppm [48]. Inhalation is the primary route for H_2S exposure. At ~30 ppm, H_2S paralyzes the sense of smell and is rapidly absorbed by the blood, resulting in poor oxygen uptake at the cellular level [49]. Some physicochemical properties of H2S is shown in Table 1.

3. Purification technologies of H_2S

Due to the numerous negative effects of H_2S, many solutions chemistry-based approaches (chemical scrubbing, precipitation, electrochemical abatement, incineration, adsorption- catalysis, catalytic conversion) and material chemistry-base approaches (zeolites, activated carbon, metal oxide nanomaterials, MOFs) have been introduced for H_2S removal. These approaches are widely used to remove H_2S from different processes.

The electrochemical method is a solution chemistry-based approach that can disintegrate H_2S in an alkaline solution. This method is based on chemical and electrochemical reactions and

precipitates the crystalline sulfur or sulfide ion at the anode and produces H_2 at the cathode [50]. During the related reactions, S^{2-} moves to the anode and is oxidized to elemental sulfur. These methods have the potential ability to remove H_2S from gas streams [51].

Table 1. Some physicochemical properties of H_2S.

Property	H_2S
Molar mass	34.08 g·mol^{-1}
Density	1.363 g dm^{-3}
Melting point	–82 °C (–116 °F; 191 K)
Boiling point	–60 °C (–76 °F; 213 K)
Vapor pressure	1740 kPa (at 21 °C)
Immediately dangerous to life or health (IDLH)	100 ppm
Threshold Limit Value (TLV)	1 ppm
Chemical structure	
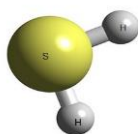
The scrubbing method includes the transfer of gaseous contaminants to the aqueous phase by providing contact between the air stream and solutions. The quantity of transferred gas depends on the concentration and solubility of gas pollutants and the resistance of the scrubber. To increase the solubility, the target component should be transformed into a water-soluble version by catalytic oxidation or alkaline conditions [52]. Scrubbing the alkaline species (OH^-, HCO_3^-, and CO_3^2) is an effective solution for removing H_2S from waste gas. It was noticed that in the presence of a high concentration of CO_2, the alkaline consumption grows, resulting in the high operating cost of scrubbing. As the alkali scrubbers have a potential for clogging and precipitation of calcium and magnesium carbonates, these scrubbers are regarded as unreliable solutions [53, 54].

Adding an oxidizing agent to the scrubbing solution improves the selectivity and removal efficiency of H_2S to this point; different oxidizing agents, including ferric ions [55], hydrogen peroxide (H_2O_2), and sodium hypochlorite, have been applied for H_2S removal [55-58]. H_2O_2 has been identified to be an effective oxidizing agent since it is inexpensive and widely available, which does not need detailed safety measures [59]. The studies classify the H_2S removal techniques into four general categories: absorption, adsorption, membranes, and cryogenic distillation [49].

3.1. Absorption by Solvent

The amine groups in the functionalized MOF can react with H_2S through an acid-base mechanism to enhance absorption. The presence of water can enhance H_2S absorption in amine-based solvents through dissolution and protonation of the amine. However, water vapor can also bind strongly and semi-reversibly to MOFs, leading to a partial reduction in their surface area. MOFs with moderate H_2S binding strengths, such as Zr-based and amine-functionalized MOFs, can exhibit reversible H_2S adsorption and absorption in the presence of solvents [59]. The addition of water can improve H_2S absorption but may also impact the MOF's stability and performance. Figure 1 shows a schematic of the absorption process of H_2S-MOF by solvent.
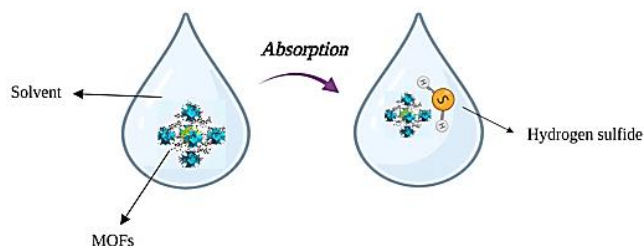

Fig. 1. Absorption of H_2S-MOF by solvent.

a) Alkanolamines
Alkanolamines are extensively utilized as chemical solvents, whereas other solvents exhibit physical properties and have a remarkably high gas absorption capacity [49]. In the past few years, diethanolamine (DEA) has been applied to remove acid gases like H_2S.

b) Methanol
Methanol is another solvent involving physical absorption at temperatures from 40°C to 60°C. Due to its low viscosity, methanol can be effectively utilized at low temperatures and under conditions of low partial pressures of gases [49]. Given the high vapor pressure of methanol, special recovery techniques, such as refrigeration, are required to

prevent significant solvent losses [60]. It is also important to consider the high costs associated with this method. Utilizing refrigeration at low temperatures requires a significant amount of power, which can contribute to increased costs [61].

c) N-Methyl-2-pyrrolidone (NMP)

Another physical absorbent is NMP. Its significantly lower vapor pressure allows it to be used at high temperatures without experiencing significant solvent loss [49]. Among the physical solvents, NMP exhibits the highest selectivity for H_2S [62].

d) Poly (ethylene glycol) Dimethyl ether (PEG-DME)

PEG-DME is another solvent known for its high viscosity, which results in a reduction of the mass-transfer rate and an increase in packing requirements, particularly at low temperatures [61]. Despite these limitations, this method benefits from low vapor pressure [49].

e) Sulfolane

Sulfolane is a physical solvent that cannot be utilized on its own and is commonly blended with chemical solvents such as alkanolamines [63]. This mixture increases the solution capacity, especially when high pressure and high concentrations are available [64].

f) Ionic liquids (ILs)

H_2S is a target pollutant in several industries, such as natural gas processing and petroleum refining, where it should be removed. ILs are highly favorable solvents for removing toxic gases, including H_2S, owing to their desirable properties, such as high thermal stability, low vapor pressure, and low melting point [51]. Currently, ILs have been used instead of alkanol amine solutions for H_2S removal as these liquid materials have specific features and can selectively remove gases. In this method, the solubility of H_2S in ILs plays a vital role in the selective separation of H_2S, and it must be taken into account [51]. The solubility of H_2S in ILs is influenced by the temperature and IL concentration. Studies have shown that the H_2S solubility increases as the mass percentage of IL is enhanced [51]. Despite the desirable features of this liquid sorbent including the diverse structure and functional groups, the preparation of it

requires expensive chemicals and multi-stage procedures [51]. Mass transport through the ILs increases operating costs. ILs have high viscosity, leading to higher power consumption [65].

g) Deep eutectic solvents (DES)

Recently, there has been extensive research on deep eutectic solvents (DESs) due to their favorable attributes, including affordability, minimal environmental impact, effortless preparation without purification requirements, and absence of byproduct formation [66]. Deep eutectic solvent (DES) is a type of ionic liquid, which is a class of liquids composed entirely of ions. Unlike traditional ionic liquids that are often synthesized from organic salts and have a fixed composition, DES are formed by mixing two or more components, typically a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA), at a specific molar ratio. The combination of these components results in a eutectic mixture, where the melting point of the resulting liquid is lower than that of each component [67].

Due to their favorable characteristics, DES are considered highly desirable solvents for the removal of H_2S. Nevertheless, the majority of the currently reported DESs, especially functionalized DESs, exhibit high viscosity attributed to the robust hydrogen-bond network within the DES structure, rendering them unsuitable for industrial H_2S removal applications. Exploring the use of aqueous and supported DESs offers an alternative approach to minimize the adverse impact of DESs' high viscosity. However, research in this area remains limited, necessitating further investigation to comprehend the roles of DESs and identify more suitable ones for effective H_2S removal [68].

3.2. Adsorption

Adsorption is attributed to the use of a selective sorbent that adsorbs one or more types of molecules of interest in a mixture. Adsorption can also be physical or chemical. Adsorption process of H_2S. Adsorption process of H_2S has been depicted in Figure 2.
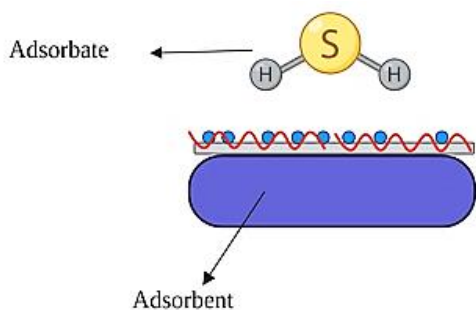
Fig. 2. Adsorption process of H_2S.

a) Metal oxides nanomaterials

Nanostructured metal oxides have a large surface area, desirable porosity, crystal structure, high interaction with gas molecules, and efficiently adsorb toxic molecules as an ideal sorbent for H_2S [69, 70]. Various nanomaterials, such as the multi-walled carbon nanotube, Fe-doped graphene nanosheet, NH-decorated graphene, impregnated carbons, ZnO nanoparticles, and reduced graphene oxide with a functionalized NH_2 group, have been applied for H_2S removal. The non-catalytic interaction of ZnO with H_2S results in the formation of ZnS and H_2O, facilitating the diffusion of H_2S [51].

b) Zeolites

Various types of zeolites with high surface area, porosity, and surface chemistry have been produced to achieve efficient removal of H_2S. Different types include all-silica zeolites, alumino-silicate zeolites, and titano-silicates. Natural zeolites act more effectively than synthetic ones, as they are economical, reusable, and have high adsorption capacity [71]. The adsorption of H_2S is influenced by temperature, with zeolites exhibiting maximum H_2S adsorption at $50℃$. The small diameter of zeolites leads to the adherence of water molecules on their surface, thereby reducing the capacity for H_2S removal. However, in some cases, this adhesion can be controlled by increasing the flow rates [51]. It was indicated that the reuse of several newly developed zeolites is not possible as the particle structure is damaged during the regeneration process [51].

c) Activated carbon

In recent years, carbon nanostructures have been developed due to their outstanding application for H_2S adsorption [72]. AC-based materials have unique features including large surface areas, good chemical properties, accessibility of internal pores, and participating in reactions through non-covalent forces [73]. These materials can use both physical adsorption and chemical oxidation for H_2S removal. To increase the removal efficiency, AC can be integrated with salts to produce metal sulfides and neutralize the H_2S. However, this may induce a decrease in the available surface area for adsorption, decreasing the removal capacity [51]. Adsorption studies have indicated that the carbon-based compounds have poor physisorption inducing the low removal efficiency of H_2S [51].

3.3. Membrane separation

Membrane technology has the opportunity to remove several components, including H_2S. Figure 3 presents a schematic of membrane for gas separation.
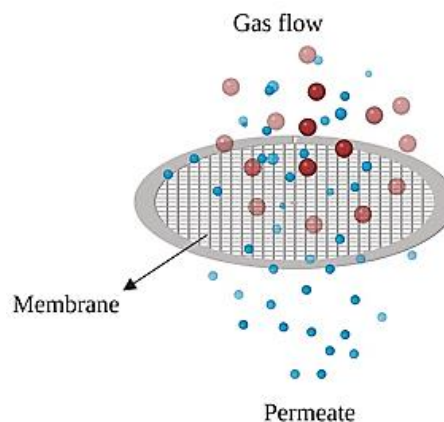

Fig. 3. Schematic of membrane for gas separation.

a) Polymeric membranes

Polymeric separation membranes represent a specific category; among them, both rubbery and glassy polymers demonstrate the ability to separate H_2S. However, rubbery polymers exhibit the most efficient performance in this regard [74]. The permeability of the membrane can be influenced by impurities. Some of the polymers also suffer from physical aging and volume reduction. The physical age of 2-5 years can also have an impact on the permeability of the membrane [74]. Polymeric membranes have drawbacks, such as their high density, which leads to low permeability [49].

b) Membranes for gas–liquid contact

Gas-liquid contact membranes offer the advantages of high surface area per unit,

independent control of flow rates for gas and liquid without any problems, mini-size, etc. [75]. One issue regarding these membranes is their unstable gas-liquid interface, which may induce insignificant performance problems in actual operation [49].

c) Ceramic membranes

Ceramic membranes are another group of membranes that control the transport properties of molecules. Polar components, such as H_2O, that may be present as an impurity, can affect membrane performance [49].

d) Carbon-based membranes

Carbon-based membranes are also effective for H_2S removal. However, these membranes have several challenges, including controlling the aggregation of individual carbon membrane units, ensuring the uniformity of thickness, and distributing of defects [49].

3.4. Cryogenic distillation

Distillation has long been considered the best choice for numerous separation purposes. However, this method has high energy consumption, requiring boiling and condensing the entire stream [49]. This method could be applied as a pre-treatment step for gas removal [76].

Another method of categorization divides the methods of H_2S removal into wet desulfurization and dry desulfurization technologies. Wet desulfurization uses amine solutions for H_2S absorption via gas-liquid acid-base reactions. The wet technology can handle high desulfurization loads but suffers from high energy consumption, equipment corrosion, low absorption rate, volatile solvent, and secondary pollution. The dry method has the advantages of high desulfurization accuracy, simple equipment, low pollution, and low energy consumption. The dry method is a chemical reaction process in which the active components of sorbents get into a reaction with H_2S, forming stable sulfides. Although dry desulfurization can remove H_2S at medium and high temperatures in high energy consumption and complex reaction conditions, it is better to operate at low temperatures [77].

MOFs have shown promising performance for the adsorption and desorption of H_2S compared to other adsorbents and absorbents.

MOFs vs Activated Carbon (AC) for H_2S Adsorption:

AC is commonly used for H_2S adsorption due to its high surface area and porous structure. Modified AC adsorbents, like dual chemical mixture (DCM) and core-shell (CS), had H_2S adsorption capacities of 0.92-1.80 mg/g. After regeneration, the CS adsorbent retained 75% of its initial capacity compared to a 62.1% loss for DCM [78].

MOFs vs Zeolites for H_2S Adsorption:

The H_2S adsorption mechanism on zeolites involves adsorption on the surface, dissolution, dissociation in pore water, and oxidation to form elemental sulfur [17]. Zeolites can be used for H_2S removal, but their performance is inferior to MOFs, which can be designed with higher surface areas and tunable pore structures [79].

Reversibility of H_2S Adsorption on MOFs:

The ability of MOFs to reversibly adsorb H_2S is challenging due to the formation of strong, sometimes irreversible bonds. Regulating the host-guest interactions between MOFs and H_2S, such as through noncovalent bonding with functionalized linkers, is key to achieving reversibility. MOFs with moderate interaction strengths, like Ni-CPO, can form reversible coordination bonds with H_2S without structural degradation [80].

In summary, while activated carbon and zeolites have been used for H_2S adsorption, MOFs offer advantages like higher surface areas, tunable pore structures, and the ability to incorporate functional groups to enhance adsorption capacity and reversibility. However, more research is needed to develop MOF adsorbents that can achieve high capacities while maintaining reversibility over many cycles for practical H_2S removal applications.

4. Synthesis methods of MOFs

The main parameters affecting the synthesis of MOFs include the reaction time and temperature, solvent selection, characteristics of metal ions and organic linkers, the size and structure of nodes, the presence of counterions, and the kinetics of crystallization. These factors collectively govern the formation of the nucleus and subsequent crystal growth during the synthesis process. The liquid

phase and mixtures of ligands and metal salt solutions are often applied to synthesize the MOFs. Factors such as reactivity, solubility, and reduction potential are considered as criteria for the suitable selection of solvent. Furthermore, the solvent type affects the determination of thermodynamics and activation energy in any reaction. For crystal growth, the reaction solution slow evaporation has often been applied. In many cases, MOF synthesis and preparation using the solvo (hydro) thermal method is a classic technique. Recently, other methods, such as mechanochemical, electrochemical, microwave, and sonochemical, have been replaced and/or developed; these methods have advantages such as lower cost, higher production speed, and higher cleaning efficiency [78-80]. The different synthesis methods of MOFs have been presented in Figure 4.

4.1. Slow evaporation (SE) and diffusion (DI) methods

The slow evaporation and diffusion methods are conducted at room temperature; these methods are not required to supply energy. In the slow evaporation method, the reagent solutions are blended and given time to evaporate slowly. Finally, crystals form if they reach a critical concentration. For process acceleration, solvents with a low boiling point are mixed [81, 82]. The diffusion method is done in two modes. The principal property of this method is the slow penetration towards the connection layer between two different environments [83, 84]. The first mode is the penetration of the liquid solvent, where two layers with different densities containing product and sediment solvent are formed. The precipitated solvent slowly penetrates the separator layer, and crystal growth occurs in the middle layer. In the other mode, it is the slow penetration of the reactants and the separation by a physical barrier. In some cases, gels are used to slow the penetration and prevent the deposition of bulk materials [85, 86]. The diffusion method is used particularly for compounds that are not very soluble [80].

4.2. Solvo (hydro) thermal (ST) method

In this method, polar solvents, such as water, alcohol, acetone, acetonitrile dimethyl formamide, diethyl formamide, etc., are used in autoclaves (closed vessels) or glass tubes under pressure and in higher temperatures than the boiling point of the solvent in the range of 50 to 260°C [87, 88]. The basic principle of the solve (hydro) thermal method is the collection and accumulation of products from a solution containing constitutive components. Furthermore, this method was originally used for the synthesis of zeolites [89]. The dominant part of MOF types has been made through the solve (hydro) thermal technique [90-92]. The autoclave containing Teflon is used to perform the reaction at high temperatures above 400°C [80]. The major advantages of this method include controlling the size, shape, and structure of the product and producing a single crystal to identify the compound. Its main disadvantages are a long time for synthesis and the non-production of pure MOFs in bulk for industrial applications [93]. One of its effective parameters on crystal growth is the cooling speed rate at the end of the reaction. Thus, so this rate should be very slow. The reaction temperature, to facilitate the bond formation and ensure the proper crystallization, may be raised [80, 88, 94].

One of the subcategories of the solve (hydro) thermal method is ionothermal synthesis. In geothermal, ionic liquids are used as solvents; these solvents have features such as low vapor pressure, high solubility for organic molecules, high thermal stability, and nonflammability, which are known as environmentally-friendly reagents and suitable solvents for the synthesis of MOFs and zeolites [95].

4.3. Microwave (MW)-assisted method

This method uses microwave radiation for heating instead of a thermal oven used in the solvo (hydro) thermal method. The advantages of the microwave method are a considerable reduction in synthesis time and proper control of particle shape and size [96, 97]. The synthesis of organic and nanoporous inorganic compounds [98], metal clusters [99], and MOF_S [100] are appropriate with this method. Ferey et al. first used this method to synthesize MIL-101; the preparation time was reported to be 60 seconds, while the synthesis by hydrothermal method takes a few days [84, 101].

4.4. Mechanochemical (MC) Method

In this approach, coordination bonds are established by employing mechanical forces, which can be applied through manual grinding or automatic ball mills. The MC method is recognized as environmentally friendly and free of solvents, although occasionally, a small amount of solvent is used to produce a high-quality polymer [102, 103]. The chief advantages of this method include high product yield, low synthesis time, no need for solvent and additional heating, high efficiency in the use of suitable raw materials, and energy saving. However, a significant drawback of this method is the absence of a readily available single crystal for determining the structure through X-ray analysis, primarily due to the formation of amorphous products [84].

4.5. Electrochemical (EC) method

In this method, the anode (target metal such as copper, cobalt, iron, etc.) and the steel cathode are placed at a short distance from each other into an electrolyte solution containing organic ligands and polar solvent to form an electrochemical cell eventually. The cell operates at a certain time and at a certain intensity of ampere and voltage to form MOF deposits. After separating the sediments and drying them, a favorable adsorbent is obtained [104]. The overriding application of the electrochemical method is the production of MOFs-powder mode on an industrial scale. The EC method, compared to the hydro thermal method, requires less temperature and synthesis time [80, 105]. HKUST-1 was the first MOF adsorbent that was synthesized by electrolysis in 2005. Today, other MOFs such as ZIF-8, MIL-100(Al), MIL-53(Al), and NH2- MIL-53(Al) are made with this technique [101].

4.6. Sonochemical (SC) method

In this method, chemical transmission occurs due to energetic ultrasonic radiation, with frequency between 20 KHz and 10 MHz [80]; the homogeneous and accelerated nuclei and crystals are formed with their synthesis time and particle diameter smaller and shorter in comparison with the hydrothermal method [106, 107]. In the SC method, the solution mixture of substrate enters the reactor fitted to a sonicator bar. After sonication, bubbles in the solution are formed and collapsed, which is called acoustic cavitation. In acoustic cavitation, too much temperature and pressure are generated, leading to very fast heating and cooling rates, eventually producing fine crystals [91]. The preparation of MOF-5 (5–25 μm size) and MOF-177 (5–20 μm size) in the presence of 1-methyl-2-pyrrolidone as a solvent is an instance of synthesis by the SC method [108, 109].

4.7. Microemulsion (ME) method

The original and common application of the microemulsion method is related to the construction of nanoparticles, and it has recently been used for the production of MOFs [110, 111]. In water microemulsions, water droplets are available on a nanometer scale that are immobilized on the organic phase via the surfactant. In microemulsions, micelles play the role of nanoreactors and are responsible for controlling the nucleus kinetics and crystal growth. The micelle's size and number depend on the surfactant type and the ratio of water to surfactant. The superior advantages of this method control the dimensions of the nano-scale compounds, but the principal disadvantages are the high cost and surfactant environmental problem [80].

4.8. Post-synthetic modification (PSM)

Researchers' efforts show that the properties of MOFs can be improved after the synthesis of compounds. The PSM of compounds is a strategic method to create functional MOFs and achieve an ideal porous compound. Chemical functionalization of MOFs, in certain ways, makes their properties controllable due to their surface modification. In PSM, the organic part of the MOF (linker) is usually changed by chemical reactions, which eventually leads to the creation of a new framework with different properties. However, the main structure of the framework does not change [83, 112].

PSM is of specific importance for the functionalization of the MOF surface because organic ligands cannot have functional groups due to instability in different synthetic conditions, such as hydrothermal, low solubility, and the possibility of coordination to metal ions [83]. In this strategy,

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the nature of the MOF cavities will change after synthesis; thus, high-sensitivity cavities are provided for the guest molecules [113].

Post-synthetic modification is divided into four groups: covalent, dative, inorganic, and ionic [114]. In covalent-PSM, a reagent is used to modify a MOF element and form a new covalent bond. The aim of the covalent-PSM is usually the MOF organic linker, but samples of this modification have been reported for the secondary building units (SBUs) [83, 115]. The dative-PSM is introduced as the use of a reactant that forms a dative bond, such as metal-ligand, with a MOF component. In this mode, either a ligand is added to SBUs or a metal origin is added to MOFs, which forms a dative bond with the organic linker in MOFs [115].

In inorganic-PSM, the compounds are metalized, and this mode is an interesting solution to improve performance in storing and separating the gases, controlling the emission of luminescence materials, activating the metal centers in the catalyst, and releasing the drugs [116]. In ionic-PSM, the opposite ion exchange (metal or cation exchange) occurs in the MOF's porous network to achieve equilibrium [83]. Therefore, the principal criterion in PSM is to replace the primary structural units (building block), which includes operations such as solvent-assisted linker exchange (SALE), non-bridging ligands replacement, and metal node replacement [80, 117]. Post-synthetic modification may lead to defects in the MOFs that can occur in metal nodes or organic linkers through replacing or missing [118].

4.9. Template strategies (TS)

The approach and strategy of template molecules usage and application as novel MOFs are still increasing dramatically [119]. In this strategy, the species that work and act as the template molecules, including small organic molecules (such as organic solvents, organic amines, carboxylic acids or carboxylates, N-heterocyclic aromatic compounds, ion liquids, surfactants, and other organic molecules), coordination compounds, polyoxometalates, biomacromolecules, block co-oligomers, polystyrene spheres, and substrate [120]. Each of these compounds has a specific role and function that affects the process of synthesis and crystallization in MOFs. For example, solvent

polarity and solubility, organic amines, and surfactant compounds impact the crystallization of the MOF, adjust the reaction solution pH, and define the shape and size of the MOFs, respectively [121]. The MOF template synthesis has two major advantages:

1. The new MOFs with a rare and unique structure and topology that were not produced by direct synthesis methods are now available.

2. The synthesis of hierarchical MOFs by template strategy is simple and easy, while the synthesis of the same MOFs by traditional methods and reticular chemistry strategy is difficult.

If the template molecules are mixed with MOF precursors, hierarchical MOFs can be prepared [122].
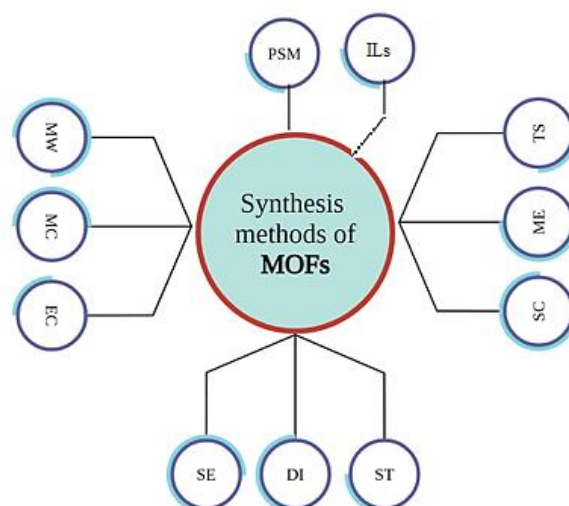

Fig. 4. Synthesis methods of MOFs. SE: Slow Evaporation, DI: Diffusion, ST: Solvo (Hydro) Thermal, MW: Microwave, MC: Mechanochemical, EC: Electrochemical, SC: Sonochemical, ME: Microemulsion, PSM: Post-Synthetic Modification, and TS: Template Strategies.

5. Results

The preliminary search yielded 414 studies across five databases. After eliminating 112 duplicate cases, the screening process was conducted on 302 studies (Figure 5). Following four stages of screening, 35 articles progressed to the final review of the results.

According to Table 2, UIO-66 was the most commonly employed MOF, utilized in nine different

studies. TOUO MOF was used eight times in various studies with different concentrations. The average pore volume for all utilized MOFs was 0.45 (cm³/g). However, it is worth noting that 21 studies did not report this particular measurement. The average temperature examined was recorded as 28.65°C, and the average H_2S absorption by MOFs across all studied cases was 14.92 mg/g.
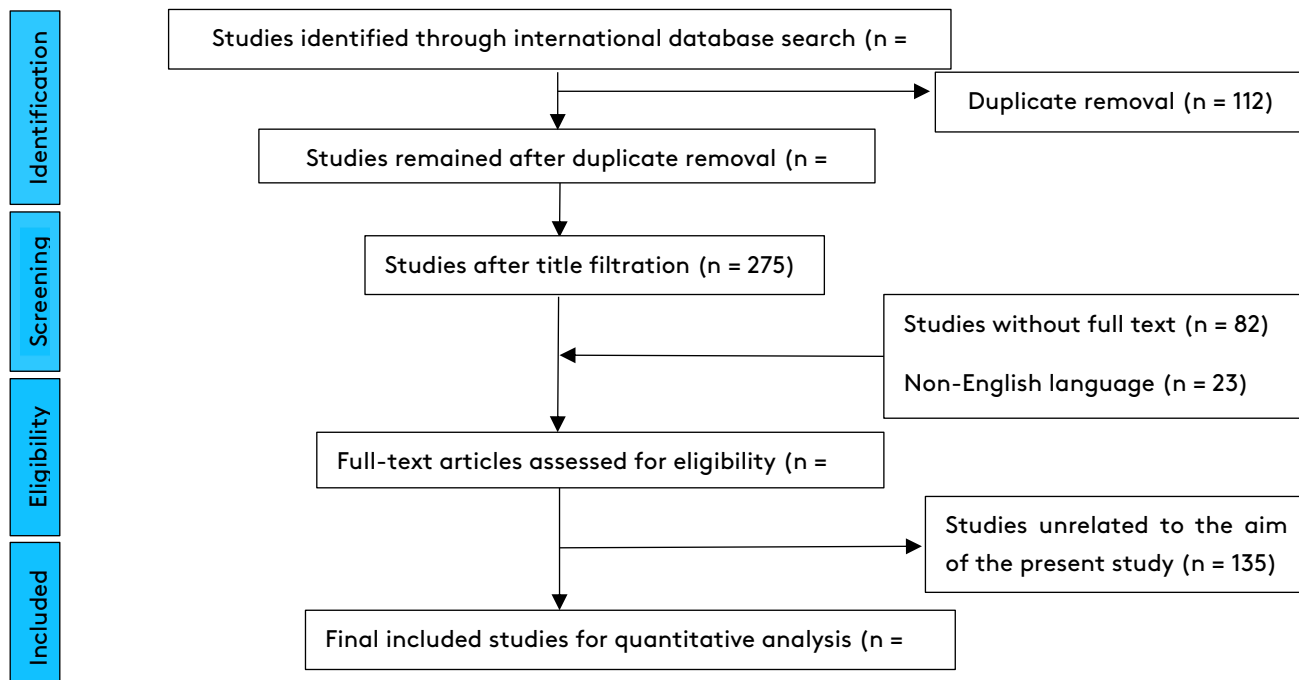

Fig. 5. Flowchart of the included studies in systematic review.

Table 2. Summary of MOF materials reported in the studies for H_2S capture.

No.	MOF	Total Pore Volume (cm³/gr)	BET Surface area (m²/g)	Gas Uptake (mg/g adsorbent)	T (°C)	P (Pa)	H_2S inlet (ppm)	Flow (ml/min)	Ref.
1	MIL-101@GCKP2-10% MIL-101@GCKP2-30% MIL-101@GCKP2-50% MIL-101	0.64 0.95 0.54 0.83	890 1084 784 1524	210.8 268.6 204 340	25	900000	-	-	[123]
2	MIL-101-HNO3-0.5 MIL-101-HNO3-1 MIL-101-HNO3-2 MIL-101-HF-1	1.41 1.72 1.25 1.52	3129 3841 2905 3609	782 923.44 612 850	25	3500000	-	-	[124]
3	HKUST-1 MGO-1 MGO-2 MGO-3	0.47 0.51 0.52 0.56	909 989 1002 996	95 200 120 110	27	760000	1000	250	[125]

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No.	MOF	Total Pore Volume (cm³/gr)	BET Surface area (m²/g)	Gas Uptake (mg/g adsorbent)	T (°C)	P (Pa)	H₂S inlet (ppm)	Flow (ml/min)	Ref.
4	UIO-66	0.44	1351	95.2 71.4 51	30 40 50	101325	4500	200	[126]
	ZMGO-3	0.47	1432	295.8 275.4 241.4	30 40 50				
	ZMGO-7 ZMGO-10	0.36 0.28	1201 1002	241.4 231.2 221 180.2 170 115.6	30 40 50 30 40 50				
5	MOF-199 (Cu-BTC) MOF-199	- 	- 	42 51.11	50 80	29	287.60	100	[127]
6	MIL-101(Cr)-powder form MIL-101(Cr)-extrudate form	1.83 1.38	3256.46 2456	247.52 137.36	25	101300	0.02 %V	67	[128]
7	MIL-101(Cr) MIL-101(Cr)- 4F(1%)	1.32 1.19	2916 2176	1020 1254.60	30	68900	15 %V	30	[129]
8	ES-ZIF-8 WS-ZIF-8	- 	- 	3298 1496	25	200000	-	42	[130]
9	UiO-66(Zr) UiO-66-NH2(Zr) MIL-125(Ti) MIL-125-NH2(Ti) MIL-101(Cr) MIL-101-NH2(Cr)	1.45	1114 963 1639 1612 2261 1288	< 17 32.3 < 17 17-27.2 17-34 -	20	-	1%V	50	[131]
10	MIL-101(Cr) MIL-101(Cr)-SO3H MIL-101(Cr)-SO3Ag	0.82 0.76 0.71	1725.24 1603.53 1534.15	24.32 28.67 96.75 76.03 71.19	20 20 20 40 60	101.32	1000	200	[132]
11	PMo₁₂@UiO-66@H₂S-MIPₛ	0.56	469	24.05	25	-	1100	100	[133]
12	GO HKUST-1 MG-1 MG-2 MG-3 MG-4 MG-5	- 0.45 0.51 0.52 0.56 0.37 0.34	- 859 989 1002 996 704 620	9 92 199 121 109 98 80	25	100000	1000	250	[134]
13	Y-FTZB-fcu-MOF Y-fum-fcu-MOF Y-1,4-NDC-fcu-MOF	0.56 0.28 0.21	1310 691 564	30.61 37.44 51	25	100000	-	-	[135]

№	MOF	Total Pore Volume (cm³/gr)	BET Surface area (m²/g)	Gas Uptake (mg/g adsorbent)	T (°C)	P (Pa)	H₂S inlet (ppm)	Flow (ml/min)	Ref.
14	UiO-66	0.44	1351	80 60 50	30 40 50	99000	4000	200	[136]
	TOUO-1%	0.38	1117	210 190 180	30 40 50				
	TOUO-3%	0.31	986	180 170 140	30 40 50				
	TOUO-5%	0.28	652	130 90 80	30 40 50				
15	Ni-CPO	0.35	1547	408	25	100000	99.5 %V	200	[137]
16	Tb-Cu-bqdc-MOF	0.27	688	48.28	25	100000	5%H₂S/ 5%CO₂/ 90%CH4	10	[138]
17	MIL-47(V) MIL-53(Cr)	0.26	654	5.6 9.4	30 30	3500 3500	99.5 %V	90	[139]
18	[Ni(NbOF5)(pyz)2]*n* (NbOFFIVE-1-Ni);	0.27	741	11.4	35	1400000	100	-	[140]
19	MIL-53 (Al)	0.54	829.9	83.98	30	107900	10	150	[141]
20	Ni-CPO	0.76	1545.32	4.70	25	101.325	100	200	[142]
21	MOF-199	0.73	1351	5.59	21	101.325	10	170	[143]
22	UiO-66-NH2 MOF-5 MOF-199	0.58 0.22 0.10	963 424 725	0.07 5.71 69	20	1	10	200	[144]
23	HKUST (Cu-based MOF) HK-01 HK-02	0.67 0.54 0.70	376 434 1380	9.31 5 16.51	25	100000	12	200	[145]
24	Ni-CPO-27	0.76	1545.32	15.90	25	1066.58	100	200	[146]
25	MIL-125(Ti) MIL-125(Ti)-NH2	0.46 0.54	1179 1244	16.09 36.88	25	100000	76	1	[147]
26	MOF-199	0.72	1250	16.7- 27.4 mol/g	25	100000	100	200	[148]
27	MOF-199/H₂S MOF-199/(H₂S + CH₃SH)	0.36 0.42	1303	23.40 12.81	25 25	0.1 0.1	43	-	[149]
28	MIL-47(V) MIL-53(Cr)	-	1145	5.62 9.43	30	3500	89	-	[150]
29	MIL-53(Al), MIL-47(V), MIL-53(Cr) MIL-53(Fe)	-	1531	6.20 63	30	3500 33000	76	-	[151]

No.	MOF	Total Pore Volume (cm³/gr)	BET Surface area (m²/g)	Gas Uptake (mg/g adsorbent)	T (°C)	P (Pa)	H₂S inlet (ppm)	Flow (ml/min)	Ref.
30	MOF-199 MOF-199 + 1%AC MOF-199 + 2%AC MOF-199 + 3.5%AC	0.51	765	56 61.51 84.63 54.60	50	36	-	-	[152]
31	MOF-199 MOF-5 UiO-66-NH2	0.38 0.57 0.46	654	69 5 0.07	25	1	69	-	[153]
32	Mg-CUK-1	0.60	586	47.62	30	68900	15 %V	30	[154]
33	MOF-199	0.54	532	73.32	200	100000	100	70	[155]
34	IRMOF-3	0.34	466	10.61	30	0.01	0.07V	56	[156]
35	MIL-100(Cr) MIL-101(Cr) MIL-47(V) MIL-53(Al) MIL-53(Cr) MIL-53(Fe)	0.62	543	568 1306 496 400 446 290	30 30 30 30 30 30	2000000 2000000 2000000 1600000 1600000 1600000	14	42	[157]
36	MOF-199 MOF-74 MIL-101 MOF-801	1.83 1.53 1.24 1.27	647	66.43 51.06 80.13 54.32	29 29 29 29	65000	72	35	[158]
37	MOF199- C1 50% MOF199- C1 10% MOF199- C1 5% MOF199- T1 50% MOF199- T1 10% MOF199- T1 5% MOF199- C2 50% MOF199- C2 10% MOF199- C2 5% MOF199- T2 50% MOF199- T2 10% MOF199- T2 5%	0.45	672	1.08 0.08 0.04 6.30 2.06 2.00 5.00 2.32 2.20 24.60 23.43 23.41	25	0.1	19	76	[159]

6. Discussion

The present study reviewed the efficiency of H₂S absorption using MOFs. MOFs are porous materials consisting of metal ions or minor metal clusters chemically bonded with multifunctional organic ligands, forming a porous framework. The diverse combination of metal centers and ligands in MOFs makes them highly suitable candidates for gas adsorption applications [149]. MOFs have been widely studied for H₂S removal purposes, and remarkable results have been observed due to the presence of metal sites and organic ligands. Each unit of MOFs serves as a potential coordination-adsorption spot for H₂S adsorption [150]. Although MOFs have shown promise in various applications, including gas adsorption, due to their high porosity, large surface area, and structural flexibility, they also have limitations and challenges when it comes to H₂S adsorption/desorption. Their key limitations are listed below, and addressing them is crucial for the effective deployment of MOFs in industrial H₂S removal applications.

Irreversible Bonding: The search results indicated that the ability of MOFs to capture H₂S molecules could be compromised by the formation of strong and sometimes irreversible bonds between the H2S

and the MOF structure [160]. This could limit the reversibility and reusability of the MOF adsorbent.

Structural Instability: Certain MOFs with open metal sites, such as HKUST-1, IRMOF-3, and MIL-53(Fe), could have their structures disintegrate when exposed to H2S, forming metal sulfides [49]. This structural breakdown reduces the effectiveness and reusability of these MOFs for H_2S removal.

Low H_2S Adsorption Capacity: Some MOF composite materials, such as MOF-GO, have been found to exhibit poor H_2S adsorption capacity despite their structural stability [161]. This limits their practical application for H_2S removal.

Lack of Understanding of Adsorption Mechanisms: The study's results highlight the need for a deeper understanding of the preferred H_2S adsorption sites within MOFs to better regulate and enhance their H_2S capture capabilities. Without this fundamental understanding, optimizing MOF performance for H_2S removal remains challenging.

Thermal Management Challenges: The exothermic nature of H_2S adsorption on MOFs could lead to sharp rises in temperature in the adsorption beds, negatively impacting their stability. There is a need to better understand the thermal properties of MOFs to design more stable adsorption systems [162].

In a pioneering study conducted by Hamon et al., the adsorption of H_2S at room temperature was investigated using various MOFs belonging to the MIL series, such as MIL-47 (V), MIL-53 (Al, Cr, Fe), MIL-100 (Cr), and MIL-101(Cr) [163]. Their findings indicated that MOFs with larger pore sizes, such as MIL-100 (16.7 mmol g^{-1}) and MIL-101 (38.4 mmol g^{-1}), generally exhibited higher adsorption capacities compared to MOFs with smaller pores, including MIL-47 (14.6 mmol g^{-1}) and MIL-53 (Al, Cr, and Fe) with respective adsorption capacities of 13.1 mmol g^{-1}, 11.8 mmol g^{-1}, and 8.5 mmol g^{-1}. Nevertheless, MIL-100 and MIL-101 MOFs, despite their large pore sizes, exhibited irreversible adsorption of H_2S. This could be attributed to either the strong interaction of H_2S with the framework or structural degradation occurring after the process of H_2S adsorption. On the contrary, MIL-47 and all MIL-53 MOFs, except for MIL-53(Fe), demonstrated complete regenerability under the same states [151].

Indeed, the type of metal used in MOFs plays a crucial role in determining the stability and reproducibility of the structure and, consequently, the absorption performance. According to the author's suggestion, the presence of hydroxyl groups at the pore openings of the MIL-53 structure creates a powerful interaction with polar H_2S molecules, resulting in pore blocking. This phenomenon contributes to the irreversible adsorption behavior observed in these MOFs.

The comparison between the calculated and experimental adsorption isotherms for H_2S on MOFs revealed that the simulated adsorption isotherm of H_2S on MOFs aligned well with the experimental data. As stated by the findings of multiple studies, the saturation plateau in the adsorption isotherms indicates the presence of a robust interaction between the adsorbent and the adsorbed. Additionally, the results indicate that the predominant absorption occurs within the material's pores and cavities. H_2S is a polar molecule with a permanent electric dipole moment, while CO_2 is a nonpolar molecule with a relatively weak electric quadrupole moment. As a result, the interaction between H_2S and the polar functional groups of MIL-47-X is notably stronger compared to the interaction of CO_2 with the same functional groups [160]. It could also be concluded that primary and secondary amines have the potential to damage the MOF structure due to the strong interaction between the nitrogen atom in the amine and copper present in certain MOFs, thus reducing the sulfur absorption capacity. On the other hand, in various studies, the modification involving the tertiary amine triethanolamine (TEA) demonstrated significantly distinct outcomes, exhibiting superior desulfurization performance compared to other MOFs. TEA-modified MOFs exhibited prolonged breakthrough times and displayed enhanced desulfurization efficiency. The microscopic arrangement of H_2S molecules within the pores of MILs indicated that during the primary stage of adsorption, H_2S can function as either a hydrogen donor (V=O $\cdots$ H-S-H) or a hydrogen acceptor (Cr-OH $\cdots$ SH_2) on MIL.

In another study conducted by Wang et al., a zinc-based MOF named IRMOF-3 containing 2-amino-1,4-benzenedicarboxylate ligand was exposed to a tertiary mixture of sulfur-containing gases. This

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mixture included dimethyl sulfide (DMS), ethanethiol (EtSH), and H_2S. In a fixed bed reactor and at room temperature, the MOF structure showed adsorption capacity equal to 16, 92.5, and 80.5 mg/g for H_2S, EtSH, and DMS, respectively [32]. Regarding the strength of the interaction between IRMOF-3 and sulfur compounds, in the case of hydrogen sulfide, the main mechanism was strong chemisorption between the sulfur atom and either the amino group (involving an acid-base interaction) or the zinc site within the MOFs. However, in the latter case, this interaction led to the production of ZnS and H_2O and could cause serious degradation of MOF. In the case of DMS and EtSH, the interactions were based on weak hydrogen bonding (an H-donor and H-acceptor mechanism) between the amino groups of the MOF and the sulfur atoms of the adsorbents, leading to lower adsorption capacities.

To gain a deeper insight into the desulfurization performance of MOFs, a research team assessed the individual contributions of different components of MOFs, including organic ligands, metal center structures, and metal ions, towards the adsorption of H_2S, DMS, and EtSH. This study was conducted using the Density Functional Theory (DFT) [161,163].

7. Conclusion

MOFs already demonstrate significant potential for H_2S removal in the present, and the outlook for these materials holds even greater promise. Advancements in MOF design, stability, regeneration efficiency, and process integration will further enhance their performance, making them more competitive and attractive for industrial-scale applications in gas purification and other separation processes. The development of cost-effective synthesis methods and broader commercialization will facilitate their widespread use, fostering a more sustainable and efficient future in the field of gas separation and purification.

Availability of data and materials

Data are available from the corresponding author upon reasonable request.

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