

High-pressure adsorption of hydrogen sulfide on MIL-53

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Abstract

Despite the growing interest in the use of biogas, the presence of contaminants such as hydrogen sulfide (H₂S) limits its application. H₂S causes damage to processing plants, the environment, and human health; therefore, it must be removed from biogas. In this context, adsorption stands out as the most efficient technique for achieving low concentrations of H₂S in purified biogas. Conventional adsorbents commonly used are zeolites and activated carbons. However, recently, metal-organic frameworks (MOFs) have attracted attention due to their wide range of possible combinations. Thus, this work aimed to synthesize and characterize the MOF MIL-53 and evaluate its performance as an H₂S adsorbent by collecting and modeling adsorption isotherms at high pressures. Synthesis of MIL-53 was confirmed by X-ray diffraction, which revealed structure characteristic peaks. Infrared spectroscopy identified functional groups and bonds typical of MIL-53. Adsorption tests demonstrated a "breathing" effect in the structure, which enhanced its adsorption capacity. A universal adsorption model was fitted to the experimental isotherms, allowing a more accurate prediction of the H₂S adsorption process on MIL-53. Additionally, the adsorbent showed excellent regeneration capacity, indicating its potential for use in cyclic adsorption processes that can be applied to purify biogas.

Keywords: Hydrogen Sulfide; Adsorption; MIL-53;

1. Introduction

Biogas, a complex mixture of gases originating from anaerobic digestion (AD), stands out as one of the most promising fuels. In addition to methane, which constitutes the primary fuel, biogas comprises other gases such as carbon dioxide and hydrogen sulfide (H₂S). H₂S notably emerges as the principal contaminant in biogas due to its ability to cause corrosion in processing facilities and its combustion, which results in the emission of toxic gases. Because of these properties, the removal of H₂S is considered the initial step in the purification of biogas. Among the methods employed to H₂S removal from biogas, adsorption proves to be the most effective when aiming to achieve the low concentrations of H₂S in biogas required by current regulations [1].

The efficiency of adsorption is closely related to the adsorbent used. Traditional adsorbents for H₂S include carbons, zeolites, and metal oxides [2]. Recent developments in metal-organic frameworks (MOFs) have expanded their use for gas adsorption [3], but there is a data gap on their application for H₂S adsorption, particularly under high pressure.

MOFs are crystalline metal-organic structures formed by the coordinated bonds of a metal cluster and an organic ligand [4]. Among the MOFs, MIL-53 appears as a flexible-structure material with great potential for gas adsorption [3] and was never tested for H₂S adsorption.

Thus, in this study, the aim was to analyze the efficiency of the MOF MIL-53 as an adsorbent for H₂S capture, through investigation and modeling of the adsorption isotherms under high pressures at various temperatures.

2. Methodology

MIL-53 structure was synthesized according to the procedure described by Loiseau et al. (2004) [4]. The synthesized material was characterized using X-ray diffraction, N₂ physisorption and Fourier-transform infrared spectroscopy (FTIR).

For obtaining the adsorption isotherms, a Rubotherm magnetic balance was used, employing the gravimetric method at temperatures of 20, 30 and 40 °C, with total pressures ranging from 10⁻⁶ to 40 bar. A preliminary activation step was performed at 200 °C for 12 h. Adsorption tests were conducted

using a synthetic mixture of helium and H₂S at 5 mol%, and the isotherms were modeled by fitting a universal model to the obtained data. This model was proposed by Ng et al. (2017) [5] and is represented by Equation (1).

$$qe = q_m \sum_i^w \alpha_i \left\{ \frac{\left(\frac{P}{P_{sat}} e^{\frac{\varepsilon_{0i}}{RT}} \right)^{\frac{RT}{m_i}}}{1 + \left(\frac{P}{P_{sat}} e^{\frac{\varepsilon_{0i}}{RT}} \right)^{\frac{RT}{m_i}}} \right\} \quad (1)$$

where q_e is the adsorbed quantity, P is the total pressure, P_{sat} is the saturation pressure, T is the adsorption temperature, and R is the universal gas constant. The model parameters were obtained by fitting the model to the experimental data using Origin® software. These parameters are: q_m , which represents the maximum adsorption capacity; ε_{0i} , which represents the adsorption energy of the site with maximum frequency; m_i , which is the standard deviation of the adsorption energy values; and α_i , which represents the probability of a molecule adsorbing on a given adsorption site.

3. Results

The synthesis of MIL-53 was confirmed by XRD, shown in Figure 1.

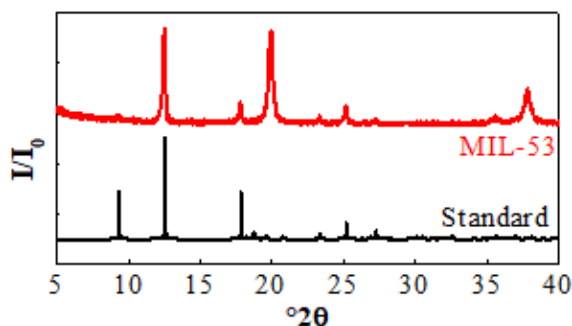


Fig. 1. X-ray Diffraction at MIL-53.

Characterization via X-ray diffraction (XRD) revealed material characteristic peaks at the expected positions, ranging from 8.93 to 34.25 °2θ, with the main peaks at 10.33 and 17.85 °2θ, as shown in Figure 1. It was observed that peaks at 19.96 and 37.8 °2θ had higher intensity than expected, which may indicate the presence of an unremoved impurity.

The N₂ physisorption isotherm displays a characteristic curve of microporous solids, classified as type 1a according to IUPAC [6]. The pore size distribution is almost monomodal, with a peak showing a maximum around 11 Å in diameter, as observed in Figure 2.

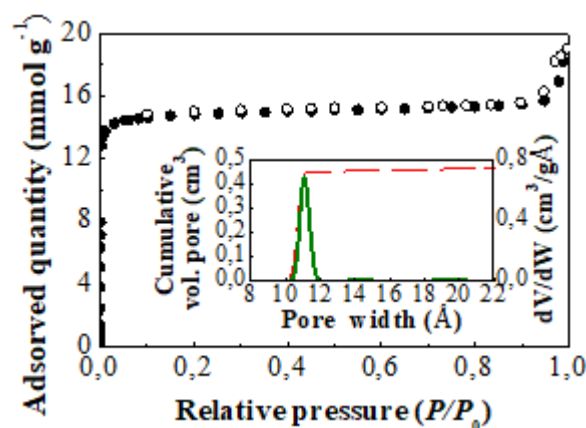


Fig.2. N₂ physisorption and pore width.

Applying the Brunauer-Emmett-Teller (BET) equation to the obtained physisorption data, a specific surface area of 1097 m²/g was obtained, with an equivalent micropore area of 1077 m²/g, highlighting the microporous nature of the material.

The infrared spectra, shown in Figure 3, revealed characteristic bands of MIL-53, including a well-defined band in the region of 3700 to 3600 cm⁻¹, attributed to the hydroxyl groups of the Al-OH bond present in the metal cluster. The region from 3000 to 2300 cm⁻¹ can be related to the presence of unreacted terephthalic acid trapped in the pores. The bands in the region of 1690 and 1630 cm⁻¹ represent the asymmetric stretching of the CO₂⁻ group, while the symmetric stretching is represented by the band at 1410 cm⁻¹, attributed to the deprotonated carboxylic group of the MIL-53 structure section.

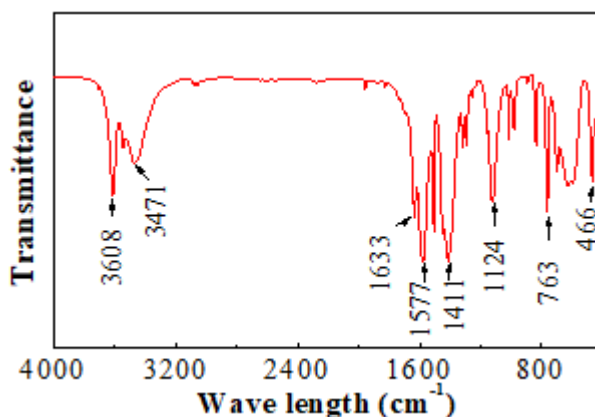


Fig.3. Infrared spectroscopy (FTIR).

The region from 1400 to 1000 cm^{-1} represents the hydrogen vibrations in the aromatic ring. Bands in the region from 1000 to 700 cm^{-1} can be associated with an Al-O bond in an AlO_4 molecule within the metal cluster.

3.1 Hydrogen sulfide adsorption

Based on adsorption isotherms shown in Figure 4, it is verified that at lower temperatures, the maximum adsorption capacity was higher.

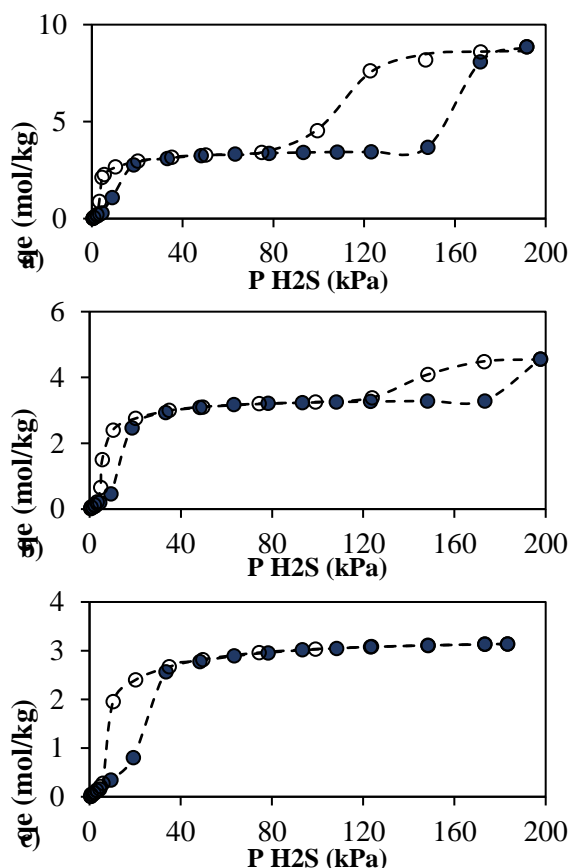


Fig. 4. Physisorption isotherms at temperatures of a) 20 °C, b) 30 °C e c) 40 °C: (---) calculated values, (●) experimental adsorption values, (○) experimental desorption values.

A greater amount of H_2S adsorbed caused a structural elongation in the adsorbent, a phenomenon known as the breathing effect [4]. This structural elongation leads to the creation of

new adsorption sites, which become occupied by additional H_2S molecules, causing a jump in the adsorbed quantity. This elongation occurs in flexible MOF's subjected to some stimulus, which can be temperature, mechanical pressure, or the adsorption of a gas [3]. The emergence of the breathing effect causes the isotherms to exhibit specific behaviors that are difficult to fit into conventional models. However, new isotherm models have been proposed, such as universal model by Ng et al. (2017) [5]. This model aims to represent the behavior of any adsorption isotherm.

The proposed model, expressed by Equation (1), considers the adsorbent surface as divided into different regions of homogeneous sites, each with its specific adsorption energy and a certain probability of binding to the adsorbent. The adsorption and desorption isotherms were fitted to the model. The calculated parameters are expressed in Table 1 for all adsorption isotherms. The fitted model showed statistical significance greater than 99%, with $p < 10^{-13}$.

Table 1. Model parameters for adsorption isotherms.

Parameter	20 °C	30 °C	40 °C
q_m	8.94	5.44	3.24
α_1	0.21	0.28	0.33
α_2	0.19	0.34	0.52
α_3	0.60	0.39	0.15
ϵ_{01}	12563.55	12433.93	11707.29
ϵ_{02}	11678.59	12376.37	12452.17
ϵ_{03}	5864.56	6162.66	13942.05
m_1	357.48	1761.69	1793.94
m_2	1913.63	120.11	245.30
m_3	71.52	21.82	2157.41
R^2	1.00	1.00	1.00

The reduction in adsorption energy (ϵ_{0i}) at sites 1 and 2 led to an increase in the probability (α_i) of molecules being adsorbed at these sites, while the opposite occurred at site 3. The experimental maximum adsorption capacities were 8.86 mol/kg, 4.56 mol/kg, and 3.13 mol/kg at temperatures of 20, 30 and 40 °C. The increase in temperature and the complete desorption of the adsorbent indicates the prevalence of physisorption and the potential for using MIL-53 in successive H_2S adsorption cycles. Three adsorption and desorption cycles were carried out with MIL-53 at 30 °C and are shown in Figure 5. The adsorption capacities in each cycle were 4.49, 4.23 and 4.44 mol/kg.

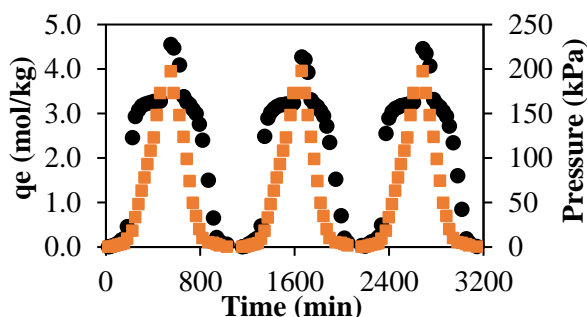


Fig. 5. Ciclos de adsorção de H₂S em MIL-5, onde ● representa a pressão e ■ a quantidade adsorvida.

Despite a slight reduction from the first to the second cycle, the adsorption capacity remained around 4.4 mol/kg up to the third cycle. Cycles performed at 20 °C may yield even more promising results. Table 3 shows the H₂S adsorption capacities of other adsorbents.

Table 3. Adsorption capacity of different adsorbents.

Adsorbent	(mol/kg)	P (kPa)	T (°C)
Activated carbon [7]	4.70	4	25
NaY [8]	6.81	4000	30
Mordenite [9]	4.11	100	25
AgII-13X [2]	0.38	100	25
USY [10]	3.68	1100	30

The adsorption capacities observed in this study, especially at 20 °C, were higher than those of other adsorbents, making MOF MIL-53 a potential adsorbent for H₂S.

4. Conclusions

In this work, MIL-53 was successfully employed as an H₂S adsorbent under high pressures. The synthesis of the adsorbent was confirmed through X-ray diffraction (XRD), infrared spectroscopy (FTIR), and nitrogen (N₂) physisorption, which revealed the distinct structural characteristics of MIL-53. Despite the observed breathing effect, the universal model applied to the experimental data effectively described the behavior of the isotherms, highlighting the efficiency of MIL-53 in H₂S removal. The profiles of the H₂S adsorption and desorption isotherms suggest that physisorption predominated during the process, and the material demonstrated a high regeneration capacity, achieving an adsorption capacity of 8.86 mol/kg. The excellent regeneration capacity observed

suggests that MIL-53 can be reused in adsorption cycles, offering a cost-effective and sustainable solution. Future research could explore optimizing operational conditions and applying MIL-53 in fixed-bed systems.

5. References

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