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## Research Article

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# Surface Diffusion–Driven Adsorption of Pyrene on Al-MCM-41: An Integrated Experimental and Phenomenological Modeling Study

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## ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental contaminants with well-documented toxic, mutagenic, and carcinogenic effects. Their recurrent presence in petroleum-derived effluents has driven the search for efficient removal technologies capable of mitigating the associated environmental risks. Consequently, the investigation of adsorbent materials and a detailed understanding of the retention mechanisms have become essential for proposing more effective remediation strategies. In this context, the adsorption and diffusion behavior of pyrene, a representative PAH, was investigated using Al-MCM-41. The heat of adsorption ( $136.1 \text{ kJ mol}^{-1}$ ) was estimated using batch experiments and compared to other previous reports. Fixed-bed column experiments, combined with simulations using a phenomenological (pore and surface diffusion) model, provided detailed mass-transfer parameters, highlighting surface diffusion as an important mechanism, especially at higher loadings. Surface diffusivity increased by nearly two orders of magnitude as the amount of adsorbed pyrene increased. Altogether, the integrated experimental and modeling results demonstrate the potential application of Al-MCM-41 as an adsorbent for pyrene removal, offering essential insights for optimizing PAH adsorption processes and contributing to the development of more effective environmental remediation strategies.

**Keywords:** Polycyclic aromatic hydrocarbons; Pyrene; Adsorption; Al-MCM-41; Pore and Surface diffusion.

## 1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are typically originated from industrial activities such as energy generation through coal combustion, coke processing, industrial operations, transportation, and waste incineration [1–5]. These compounds may enter the surface water through discharges from industrial facilities and wastewater treatment plants, while soils in waste disposal areas are often contaminated due to inadequate storage conditions [6–8]. The effects of human exposure to PAHs depend on the duration and intensity of contact, their concentration and intrinsic toxicity, and the route of exposure, whether inhalation, ingestion, or dermal contact. Additionally, PAHs have the potential to cause harm to wildlife and vegetation, with cumulative effects on exposed [9–11].

Several studies have focused on the removal of PAHs from various sources, including hot gas emissions [12], contaminated soils [13,14], and industrial effluents or solvents [15,16]. Among the investigated process options, adsorption stands out due to its low energy demand and potential for adsorbent regeneration [17,18]. Furthermore, mesoporous material has demonstrated potential effectiveness if compared to traditional activated carbon adsorbents [19–21]. Therefore, understanding the diffusion mechanisms of the PAHs within these mesoporous materials may be important for optimizing the pollutants removal processes and expanding their industrial applications.

MCM-41 was developed as an alternative for the adsorption and/or reaction of bulky molecules requiring mesoporous channels. Composed of an amorphous silica wall, it exhibits a long-range ordered structure with uniform mesopores and surface areas exceeding 1000 m<sup>2</sup> g<sup>-1</sup> [22–24]. Furthermore, pore diameters may be tuned within the 1.5–20 nm range by optimizing synthesis conditions and employing surfactants with different chain lengths [25–27]. The adsorption potential of MCM-41 has been extensively explored in various applications, including the removal of metals and basic dyes from aqueous solutions [28–30],

as well as the capture of volatile organic compounds [31,32]. Studies have also demonstrated its potential for PAHs adsorption [33,34] and the treatment of aqueous solutions containing monoaromatic compounds [35–37], highlighting the versatility and adsorption capabilities of this material.

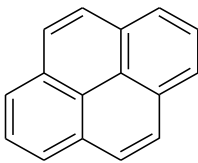
In this study, a sample of Al-MCM-41 was synthesized and evaluated as an adsorbent for the retention of pyrene, selected as a representative PAH molecule. Batch experiments were conducted to assess the adsorption equilibrium behavior in liquid phase, while fixed-bed column tests were used to examine the adsorption dynamics under flow conditions. In addition, a computational approach was employed to simulate the breakthrough curves using a phenomenological model to estimate the mass-transfer parameters associated with the process. Thus, the set of experimental and simulation results obtained may contribute in an integrated way to the development of strategies for the removal of PAHs.

## 2 Experimental and modeling

### 2.1 Materials

Al-MCM-41 was synthesized utilizing the following reagents: silica gel (Aldrich, 95.5%), sodium hydroxide (Vetec, 99%), cetyltrimethylammonium bromide (CTMABr, Vetec, 98%), pseudoboehmite (Vista, 68%  $\text{Al}_2\text{O}_3$ ), and acetic acid (Vetec, 30%), all dissolved in distilled water. Pyrene (Acros Organics, >98% purity, USA) was employed as the reference PAH. The structural and physicochemical properties of pyrene are summarized in Table 1. HPLC-grade iso-octane (J.T. Baker, >99% purity, USA) served as the solvent. Gases, including hydrogen, nitrogen, synthetic air, and helium, were obtained from White Martins Praxair (Brazil).

**Table 1.** Structural characteristics and physicochemical properties of pyrene.

| PAH                                                            | Pyrene                                                                               |
|----------------------------------------------------------------|--------------------------------------------------------------------------------------|
| Structure                                                      |  |
| Molecular weight ( $\text{g mol}^{-1}$ )                       | 202.26                                                                               |
| Boiling point ( $^{\circ}\text{C}$ )                           | 360                                                                                  |
| Molar vol. at boiling point ( $\text{cm}^3 \text{gmol}^{-1}$ ) | 213.8                                                                                |
| Kinetic diameter (nm)                                          | 0.75                                                                                 |

### 2.2 Synthesis of Al-MCM-41

The Al-MCM-41 sample was synthesized hydrothermally, using aqueous solutions of NaOH,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  as the aluminum source. These solutions were mixed with distilled  $\text{H}_2\text{O}$  and stirred for 2 h at 60  $^{\circ}\text{C}$ . The synthesis of Al-MCM-41 had the following ratio of gel composition: 17.1CTMABr: 3.7NaOH: 11.122 $\text{SiO}_2$ : 165 $\text{H}_2\text{O}$ : 1 $\text{Al}_2\text{O}_3$ , with Si/Al

approximately 5. Thereafter, an aqueous solution of CTMABr as a structure-directing template was prepared under constant agitation for 30 min. Then, the two solutions were mixed and placed into a teflon container and submitted to hydrothermal treatment at 80 °C for 5 days. The pH was adjusted to the range between 9-10 with a 30% acetic acid solution. The sample was then filtered, washed with H<sub>2</sub>O and dried at 26 °C and finally calcined at 550 °C to remove the surfactant. For the subsequent adsorption experiments, the samples were previously heated at 120 °C for at least 24 h in an inert-atmosphere oven to remove moisture and other contaminants.

### 2.3 Characterization of the Al-MCM-41 sample

The crystallinity and phase purity of the synthesized material were determined using X-ray diffraction (XRD), performed on a PANalytical X'Pert diffractometer (UK) with Cu K $\alpha$  radiation. Diffractograms were registered for low angle ( $\leq 10^\circ$ ) at a rate of 5°C min<sup>-1</sup>. Fourier transform infrared spectroscopy (FTIR) was employed to investigate the chemical bonds of Al-MCM-41, using an Agilent Cary 630 FTIR spectrometer (USA). The sample was prepared in KBr, and spectra were recorded between 4000 and 420 cm<sup>-1</sup>. Nitrogen adsorption-desorption isotherms at -195°C were obtained using a Quantachrome Autosorb-1 MP (USA). Specific surface area and pore size distribution were calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. The total pore volume was determined from the N<sub>2</sub> volume adsorbed at a relative pressure of 0.95, following the procedure described by [38]. Micrometric-scale images were acquired via scanning electron microscopy (SEM) using a FEI Quanta 450 FEG microscope (USA) operating at 5 kV. Samples were coated with gold prior to imaging.

### 2.4 Batch adsorption experiments

Equilibrium measurements in liquid phase were performed at 30, 45, and 60 °C and under constant agitation. Al-MCM-41 sample (0.1 g each) was put in contact with solutions

containing different sorbate concentrations (1 to 15 mmol L<sup>-1</sup>) of pyrene in iso-octane. After reaching equilibrium (approx. 24 hours), the solution was separated from the Al-MCM-41 by filtration and pyrene concentrations measured using a Varian CP-3800 with an FID detector (USA). Information about the column, calibration range, detection limits, and linearity of pyrene in isooctane solution is presented in Table 2.

**Table 2.** Calibration data for pyrene using the GC-FID method.

| PAH                                       | Pyrene               |
|-------------------------------------------|----------------------|
| Column                                    | CP-Sil 8CB capillary |
| Calibration range (mmol L <sup>-1</sup> ) | 0.1-15               |
| Reg. equation                             | y=0.22x+75.49        |
| Linearity (R <sup>2</sup> )               | 0.982                |
| Detection limit (mmol L <sup>-1</sup> )   | 0.01                 |

The apparent equilibrium concentrations of pyrene in the adsorbed phase ( $q^*$ ), assuming negligible adsorption of iso-octane compared to pyrene in this system, were calculated using Eq. 1.

$$q^* = \frac{V_S (C_0 - C_e)}{M_A} \quad (1)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of pyrene in the iso-octane solution (mmol L<sup>-1</sup>), respectively;  $V_S$  is the volume of the solution (L); and  $M_A$  is the weight of the solid sample (g). For the calculation of concentrations in the adsorbed phase, it was considered that the adsorption of isooctane is negligible when compared to that of pyrene in this scenario. Each experimental data point was obtained from duplicate measurements.

The apparent equilibrium adsorption data were fitted using Langmuir and Toth isotherm equations (Eq. 2 and 3, respectively).

$$\frac{q^*}{q_m} = \frac{b_L C_e}{1 + b_L C_e} \quad (2)$$

$$\frac{q^*}{q_m} = \frac{C_e}{(b_T + C_e^v)^{1/v}} \quad (3)$$

In these equations,  $b_L$  is the Langmuir constant,  $q_m$  is the maximum adsorption capacity for a given temperature,  $b_T$  is a parameter indicative of the adsorbent affinity for the adsorbate, and  $v$  is a parameter related to the degree of heterogeneity of the adsorbent surface.

The apparent adsorption energies ( $-\Delta U_{ap}$ ) were estimated using the van't Hoff equation (Eq. 4).

$$\ln K = \ln K_0 - \frac{\Delta U_{ap}}{RT} \quad (4)$$

$K$  is the adsorption constant in the Henry's Law region, estimated from the virial plot of the equilibrium data, according to Eq. 5 [39], using a semi-log plot of  $C_e/q^*$  versus  $q^*$ , following the virial equilibrium isotherm:

$$\frac{C_e}{q^*} = \exp(A_0 + A_1 q^* + A_2 q^{*2} + A_3 q^{*3} + \dots) \quad (5)$$

In Eq. 4,  $K_0$  is a pre-exponential factor,  $\Delta U_{ap}$  is the apparent energy of adsorption,  $T$  is the absolute temperature, and  $R$  is the universal gas constant.

The adsorption enthalpy ( $\Delta H_{ads}$ ) was then calculated (Eq. 6) by applying the thermodynamic relationship between internal energy ( $U$ ) and enthalpy ( $H$ ), while also accounting for the solvent adsorption enthalpy ( $-\Delta H_{sol}$ ). This takes into account the enthalpy related to the solvent co-adsorption and subsequent displacement by the aromatic compound.

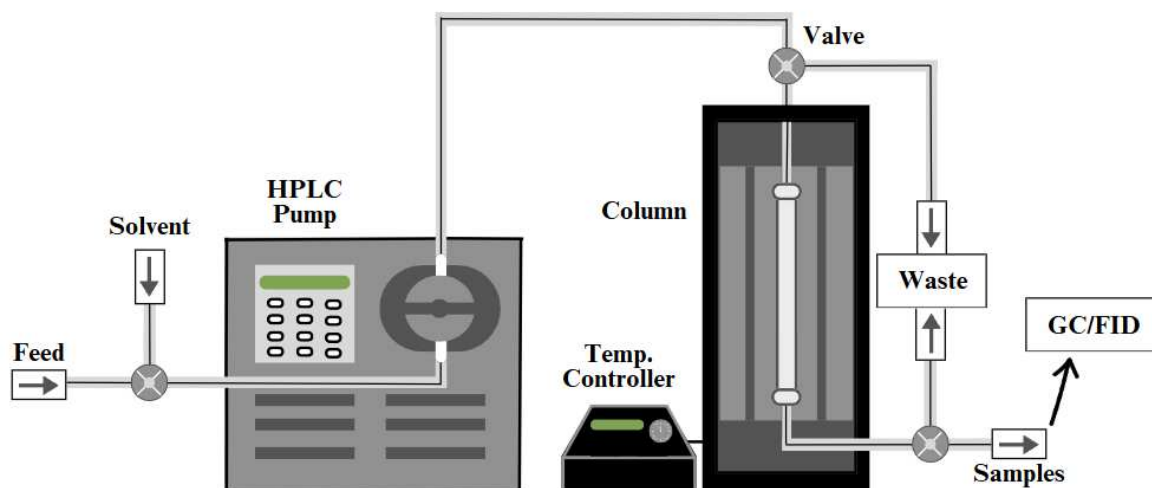
$$\Delta H_{ads} = \Delta U_{ap} + \Delta H_{sol} - RT \quad (6)$$

The heat of adsorption of the solvent ( $-\Delta H_{sol}$ ) was assumed to be equivalent to that of n-octane, as reported by Kalies *et al.* [40]. This assumption accounts for the co-adsorption of the solvent, followed by its displacement by the aromatic compound (pyrene). Thus, in calculating the enthalpy of adsorption ( $\Delta H_{ads}$ ), the contribution associated with solvent adsorption ( $-\Delta H_{sol}$ ) was incorporated to adequately account for the displacement effect during pyrene adsorption.

## 2.5 Adsorption experiments in a fixed-bed column

Column experiments were conducted using a Varian ProStar 210 HPLC system (USA), as depicted in Fig. 1. The column was under temperature control using an Eldex Laboratories CH-150 oven (USA), from 5 to 150°C  $\pm$  0.1°C. Initially, a stable baseline flow of pure iso-octane was established to ensure steady flow rates through the column. Subsequently, two separate experiments were performed, employing feed solutions with pyrene concentrations of 0.17 mmol L<sup>-1</sup> and 3.57 mmol L<sup>-1</sup>, respectively. Samples were collected at the column outlet at regular intervals to measure the pyrene concentrations. All column experiments were performed at 30°C. The pyrene concentrations were also quantified by gas chromatography-flame ionization detection (GC-FID).

**Fig. 1.** Experimental setup used for the breakthrough experiments.



The solid phase concentration in equilibrium was calculated from the breakthrough curves for each experiment, at initial concentration ( $C_o$ ), using Eq. 7.

$$q^* = \frac{C_o}{M_B} \left[ Q \int_0^t \left( 1 - \frac{C}{C_o} \right) dt - V_C \varepsilon \right] \quad (7)$$

where  $C$  is the concentration in bulk ( $\text{mg g}^{-1}$ ),  $M_B$  is the adsorbent bed weight (g),  $V_C$  is the column volume ( $\text{cm}^3$ ) and  $\varepsilon$  is the bed porosity.

## 2.6. Modeling, simulation and estimation of corrected surface diffusivities

The pore and surface diffusion model [41, 42] was employed to predict the breakthrough curves and validate the experimental data for estimation of surface diffusivities ( $D_S$ ) using Eq. 8-14.

Differential mass balance in liquid phase:

$$\varepsilon \frac{\partial C}{\partial t} + u \frac{\partial C}{\partial z} = \varepsilon D_L \frac{\partial^2 C}{\partial z^2} - (1 - \varepsilon) \frac{3k_f}{R} \left( C - C_p \Big|_{r=R_p} \right) \quad (8)$$

Initial conditions:

$$t = 0, \quad C(z, 0) = C_{n-1}, q(z, 0) = q_{n-1} \quad (9)$$

Boundary 1:

$$z = 0, \quad uC(0, t) - D_L \frac{\partial C}{\partial z} = u(C_n - C_{n-1}) \quad (10)$$

Boundary 2:

$$z = L, \quad \frac{\partial C(L, t)}{\partial z} = 0 \quad (11)$$

Differential mass balance in solid phase:

$$\varepsilon_p \frac{\partial C_p}{\partial t} + (1 - \varepsilon_p) \frac{\partial q}{\partial t} \rho_{ap} = D_p \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_p}{\partial r} \right) + D_S \frac{\rho_{ap}}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial q}{\partial r} \right) \quad (12)$$

Boundary 1:

$$r = 0, \quad \frac{\partial C_p}{\partial r} = 0 \quad (13)$$

Boundary 2:

$$r = R_p, \quad D_p \frac{\partial C_p}{\partial r} + D_S \frac{\partial q}{\partial r} \rho_{ap} = k_f (C - C_p) \quad (14)$$

where  $C_p$  represents the intra-particle liquid-phase concentration, and  $q$  is a function of  $C_p$  calculated using the Toth equation (Eq. 3), derived from batch experiments.

The gPROMS commercial simulator was used to numerically solve this model. This system of partial differential and algebraic equations (DAE) were discretized in the axial and radial using a third-order orthogonal collocation method in finite elements (OCFEM). The mass transfer parameters of the fixed-bed system ( $D_s$ ) were estimated using an optimization package based on the heteroscedastic method, version 3.2 [43].

The root mean squared error (RMSE) was used to evaluate the fitting of the model to the experimental data, as shown in Eq. 15.

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (C_{Sim} - C_{Exp})^2} \quad (15)$$

where  $C_{Sim}$  is the concentration estimated from the model,  $C_{Exp}$  is the experimental concentration and  $N$  is the number of measured values. A  $RMSE = 0$  indicates a perfect model prediction of the experimental data.

The axial dispersion coefficients were estimated using an empirical correlation [44]:

$$\varepsilon \frac{D_L}{u d_p} = 0.2 + 0.011 Re^{0.48} \quad (16)$$

The external film mass transfer coefficient ( $k_f$ ) was determined using the correlation proposed by [45]:

$$Sh \equiv \frac{d_p k_f}{D_m} = 2 + 1.1 (Sc)^{1/3} (Re)^{0.6} \quad (17)$$

The molecular diffusivities ( $D_m$ ) of the PAH were estimated from the Wilke and Chang correlation [46]:

$$D_m = 7.4 \cdot 10^{-8} \frac{(\varphi M)^{1/2} T}{\eta V_b^{0.6}} \quad (18)$$

where  $M$  ( $\text{g mol}^{-1}$ ) denotes the molecular weight,  $\eta$  (cP) represents the solution viscosity,  $T$  (K) is the absolute temperature, and  $V_b$  ( $\text{cm}^3 \text{mol}^{-1}$ ) corresponds to the molar volume at the normal boiling point. It is worth noting that the parameter  $\phi$  is an association coefficient, assumed to be 1.0 for aromatic compounds.

The pore diffusion coefficient was calculated from the estimated molecular diffusivity (Eq. 19), incorporating a tortuosity factor of 5.0, a value commonly observed in similar systems [39,47].

$$D_p = \frac{D_m \varepsilon_p}{\tau} \quad (19)$$

The Darken equation was employed to assess the influence of equilibrium conditions on the surface diffusion coefficients results [48]. The loading dependency of the surface diffusivity was predicted using Eq. 20.

$$D_S = D_{S0} \frac{d \ln C}{d \ln q} \quad (20)$$

This correction may be expressed, provided the equilibrium is represented by the Langmuir isotherm (Eq. 21) or the Toth isotherm (Eq. 22).

$$D_{S0} = D_S \left( 1 - \frac{q^*}{q_m} \right) \quad (21)$$

$$D_{S0} = D_S \left( \frac{1}{1 + (b_T C_p)^v} \right) \quad (22)$$

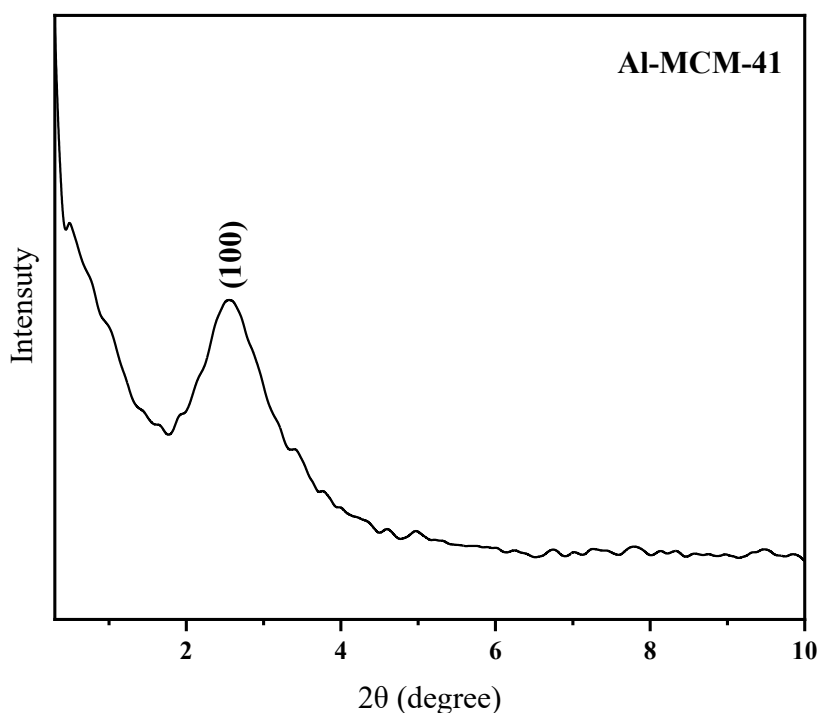
where  $D_{S0}$  is the corrected surface diffusivity and  $d \ln C / d \ln q^*$  is called the thermodynamic correction factor.

### 3 Results and discussion

#### 3.1 Characterization of Al-MCM-41

The X-ray diffractogram for the Al-MCM-41 sample (Si/Al  $\sim$  5) corresponds to that observed for the formation of mesoporous hexagonal structure, as shown in Fig. 2. A characteristic peak may be observed at  $2.6^\circ$ , corresponding to the Miller index (100), with a higher intensity. A similar behavior was observed by Park *et al.* [49] when they reported the difference in the structure of pure MCM-14 from Al-MCM-41.

**Fig. 2.** XRD pattern for Al-MCM-41.



In this previous study, the authors observed a decrease in the intensity of the peaks when incorporating Al into the structure of MCM-41. More specifically, the decrease in the intensity of these peaks after an increase in the amount of Al incorporated (e.g., with a decrease in the Si/Al ratio), was attributed to an increase in the size of the pores, leaving the peaks wider and with less intensity. Thus, the incorporation of aluminum into Al-MCM-41

generates acidic sites that favor interaction with aromatic molecules, resulting in regions with different interaction energies on the pore surface.

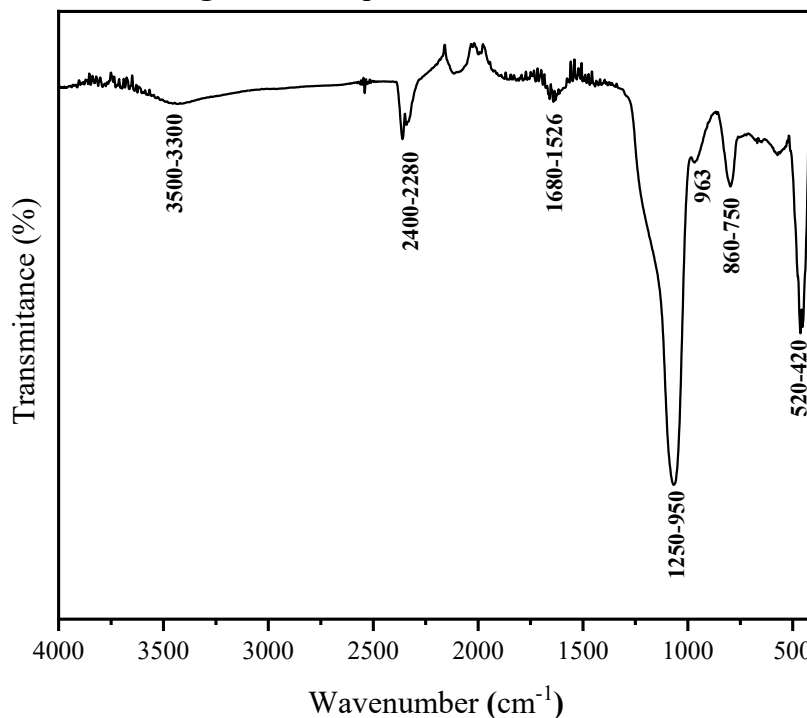
The low-angle X-ray diffraction pattern of Al-MCM-41 exhibits a characteristic reflection at approximately  $2\theta = 2.6^\circ$ , which is indexed to the (100) crystallographic plane. This reflection is characteristic of the ordered mesoporous MCM-41 structure and is associated with the two-dimensional hexagonal arrangement of channels with  $p6mm$  symmetry. Furthermore, it may also be attributed to the presence of long-range structural periodicity in the mesoporous structure. The reflection, assigned to the (100) plane, indicates the presence of long-range structural periodicity within the mesoporous framework. However, a certain degree of broadening may be observed, which may be attributed to the incorporation of aluminum into the silicate framework, the relatively low crystallinity of the amorphous silica-alumina pore walls, and the presence of structural defects.

This behavior is consistent with the results reported for Al-MCM-41 materials, where the low-angle reflections confirm the formation of an ordered mesoporous structure, while aluminum incorporation generates acidic sites without significantly disrupting the hexagonal arrangement of the support [50,51]. Furthermore, studies by Araujo *et al.* [52] demonstrated that Al-MCM-41 retains its mesostructural ordering after aluminum incorporation and exhibits acidity strongly dependent on the Si/Al ratio, making this material highly suitable for catalytic applications and the adsorption of bulky molecules. Therefore, the XRD results confirm that the sample possesses the typical Al-MCM-41 structure, characterized by ordered mesoporous channels, a hexagonal arrangement, and successful aluminum incorporation, which is associated with the generation of Brønsted and Lewis acid sites.

With the infrared spectrum seen in Fig. 3, it was possible to identify peaks in the range of  $3500\text{--}3300\text{ cm}^{-1}$  that may be attributed to the silanol groups and adsorbed water of Al-MCM-41. Already in the region of  $1680\text{--}1526\text{ cm}^{-1}$ , it may be attributed to vibrations of

deformation of adsorbed molecules. Furthermore, the vibrations attributed to the tetrahedron T-O-T (T=Si, Al) may be seen in the range of 1250-950  $\text{cm}^{-1}$ . The symmetrical and asymmetrical stretches of the T-O bonds (T = Si, Al) may be assigned to the adsorption bands 860-750  $\text{cm}^{-1}$  and 520-420  $\text{cm}^{-1}$ , respectively [53].

**Fig. 3.** FT-IR spectra of Al-MCM-41.



The FTIR spectrum of Al-MCM-41 exhibits the characteristic vibrational bands of mesoporous aluminosilicate materials belonging to the MCM-41 family. The broad band observed in the 3500–3300  $\text{cm}^{-1}$  region is assigned to the stretching vibrations of surface hydroxyl groups (Si–OH and Al–OH) and adsorbed water molecules. The band located between 1680 and 1526  $\text{cm}^{-1}$  is associated with the bending vibration of water molecules confined within the mesoporous channels. Such bands are commonly observed in Al-MCM-41 materials due to their high surface area and large concentration of silanol groups [51]. The most intense absorption region, between 1250 and 950  $\text{cm}^{-1}$ , corresponds to the asymmetric stretching vibrations of the siloxane framework (Si–O–Si). Within this region, the band centered at approximately 963  $\text{cm}^{-1}$  is particularly important because it is commonly

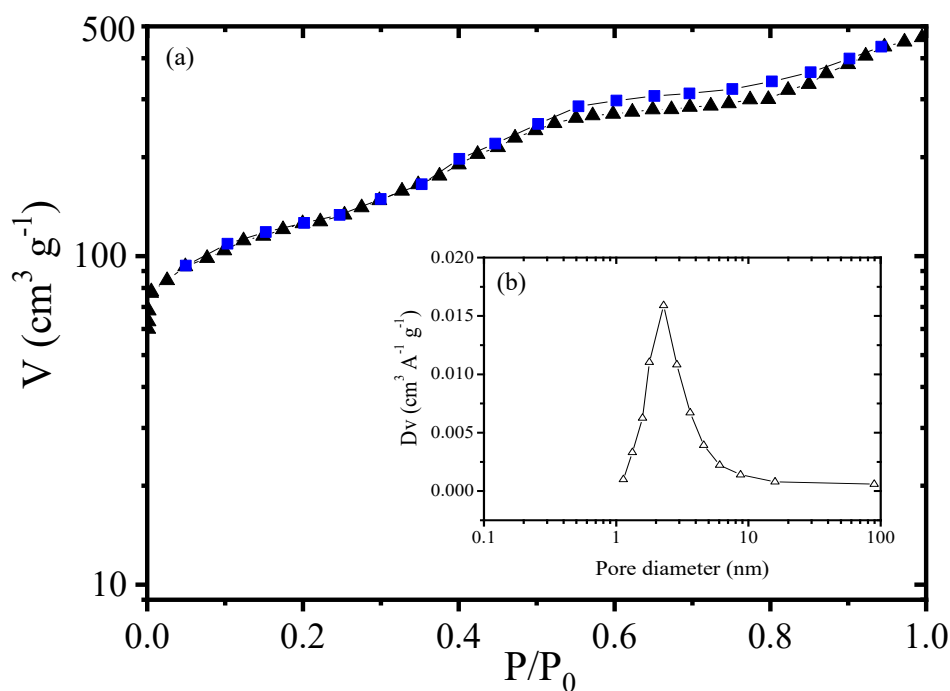
1 attributed to Si–O–Al linkages or to Si–OH groups perturbed by neighboring tetrahedrally  
2 coordinated aluminum species. This band is widely recognized as evidence of the successful  
3 incorporation of aluminum into the silica framework, leading to the generation of acidic sites  
4 within the mesoporous structure [50]. The bands observed in the 860–750 cm<sup>-1</sup> region are  
5 attributed to the symmetric stretching vibrations of Si–O–Si bonds, whereas the absorption  
6 band in the 520–420 cm<sup>-1</sup> region corresponds to the bending vibrations of tetrahedral units  
7 (T–O–T, where T = Si or Al). These features confirm the preservation of the mesoporous  
8 aluminosilicate framework after aluminum incorporation and calcination [52].

9         Furthermore, the absence of significant bands in the 2920–2850 cm<sup>-1</sup> region indicates  
10 the effective removal of the cetyltrimethylammonium bromide (CTMABr) template during  
11 calcination. This observation is consistent with previous studies conducted by Araujo *et al.*  
12 [54], who investigated the thermal decomposition and removal of surfactant molecules from  
13 Al-MCM-41 using thermogravimetric and kinetic analyses. Overall, the FTIR spectrum  
14 confirms the successful synthesis of Al-MCM-41, the incorporation of aluminum into the  
15 silica framework, and the formation of Brønsted and Lewis acid sites. These structural and  
16 acidic characteristics are essential for applications involving adsorption, catalytic cracking,  
17 hydrocarbon conversion, and adsorptive desulfurization of petroleum-derived fuels [51].

18         N<sub>2</sub> adsorption isotherms of the Al-MCM-41 sample are shown in Fig. 4a, displaying  
19 typical characteristics of mesoporous materials, with an initial low-pressure region  
20 corresponding to monolayer adsorption, in which the N<sub>2</sub> molecules interact directly with the  
21 internal pore surface, followed by multilayer formation with increasing relative pressure  
22 (IUPAC type IV). The observed hysteresis confirms the presence of mesopores, reflecting the  
23 occurrence of capillary condensation and evaporation at different relative pressures within the  
24 porous structure [55].

The N<sub>2</sub> adsorption–desorption isotherm of Al-MCM-41 exhibits a typical type IV profile with a capillary condensation step at intermediate relative pressures, confirming the mesoporous nature of the material. The sharp increase in nitrogen uptake at  $P/P_0 \approx 0.35\text{--}0.60$  is associated with capillary condensation within uniform cylindrical mesopores. The pore size distribution shows a narrow maximum centered at approximately 2.8 nm (see Fig. 4b), indicating a highly ordered pore system with excellent structural homogeneity. These results are consistent with the low-angle XRD pattern, which displays the characteristic (100), (110), and (200) reflections of the hexagonal  $p6mm$  structure.

**Fig. 4.** (a) Adsorption (▲) and Desorption (■) isotherms of N<sub>2</sub> at 77 K for the Al-MCM-41 sample; and (b) pore size distribution of the Al-MCM-41 sample (BJH method).



The preservation of mesostructural ordering after aluminum incorporation demonstrates that framework substitution occurred without significant collapse of the mesoporous architecture. Similar behavior has been reported by Araujo *et al.* [50] and Costa *et al.* [51] for Al-MCM-41 materials prepared by direct synthesis and post-synthesis

alumination, where pore diameters between 2 and 4 nm and high surface areas were obtained while maintaining the characteristic hexagonal arrangement of channels.

The pore size distribution estimated using the BJH method, displaying a well-organized mesoporous network, with pore diameters between 1 and 10 nm [56]. This distribution indicates the presence of both primary mesopores associated with the expected hexagonal arrangement of the Al-MCM-41 structure and secondary pores that may be attributed to slight structural variations. The coexistence of these porous domains results in a hierarchical system that enhances diffusion and increases internal surface accessibility, features that are particularly relevant for adsorption processes involving large molecules such as pyrene.

The estimated textural parameters are summarized in Table 3. The pores surface area of  $540 \text{ m}^2 \text{ g}^{-1}$  reflects the external and internal surface exposure, providing a broad interface for adsorbate-surface interactions. The total pore volume of  $0.560 \text{ cm}^3 \text{ g}^{-1}$  indicates a substantial void fraction within the material, which is essential not only for accommodating adsorbed molecules but also for facilitating intraparticle transport due to the connectivity of the pore network.

**Table 3.** Textural properties of Al-MCM-41.

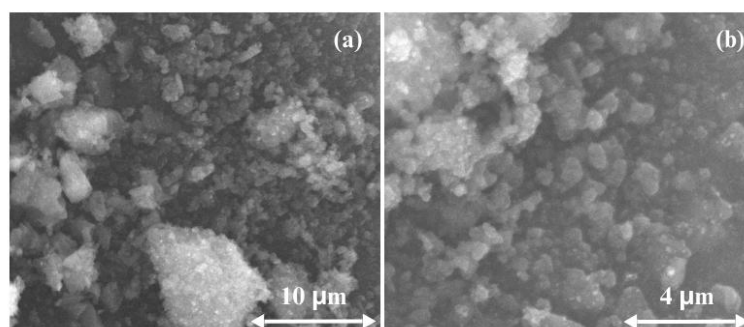
| Properties                                         | Al-MCM-41 |
|----------------------------------------------------|-----------|
| Surface area ( $\text{m}^2 \text{ g}^{-1}$ )       | 540       |
| Total pore volume ( $\text{cm}^3 \text{ g}^{-1}$ ) | 0.560     |
| Particle porosity                                  | 0.41      |

The particle porosity, estimated at 0.41, reflects the proportion of internal voids available for molecular transport. This parameter, particularly in dynamic systems, directly influences the shape of breakthrough curve, as it is associated with the effective porosity used

in fixed-bed modeling. Thus, the combination of high surface area, substantial pore volume, and adequate particle porosity demonstrates that the synthesized Al-MCM-41 sample provides a favorable environment for adsorption and diffusion processes, justifying its selection for the experimental and computational investigations that were carried out.

Through the SEM images shown in Fig. 5, it is possible to observe a homogeneous morphology and a well-ordered particle structure. The synthesized sample exhibited elongated particles with a rounded shape and, in some cases, hexagonal features. In addition, good particle dispersion may also be observed. Thus, the SEM images confirm a sample with appropriate morphology and structure, consistent with typical Al-MCM-41.

**Fig. 5.** SEM images of the Al-MCM-41 sample, at magnifications of (a) 10,000 $\times$  and (b) 25,000 $\times$ .



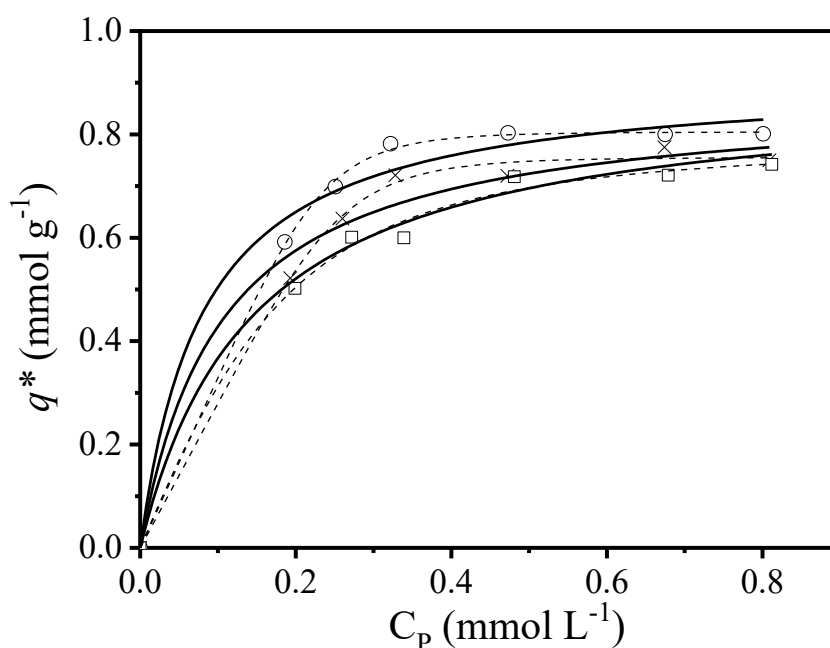
The SEM images of Al-MCM-41 (Fig. 5) reveal a morphology consisting of irregular agglomerates formed by the assembly of submicrometric primary particles. At lower magnification, the material exhibits aggregates with dimensions of several micrometers, whereas higher magnification reveals that these aggregates are composed of nearly spherical to irregular nanoparticles. No well-defined crystalline faces are observed, which is consistent with the nature of the silica–alumina pore walls characteristic of MCM-41 materials. The rough surface texture and homogeneous particle distribution suggest the presence of an extensive mesoporous network and indicate that aluminum incorporation did not significantly alter the morphology of the support. The preservation of particle morphology, together with

the ordered mesostructure evidenced by XRD and the narrow pore size distribution obtained from N<sub>2</sub> adsorption measurements, confirms the successful synthesis of highly ordered Al-MCM-41 suitable for catalytic and adsorption applications. In particular, the Si/Al  $\approx$  5 ratio provided a well-organized mesoporous structure with a suitable surface area and acid sites, which are important characteristics for adsorption applications.

### 3.2 Batch adsorption experiments

The apparent adsorption isotherms of pyrene on the Al-MCM-41 sample, in iso-octane solution, are shown in Fig. 6, for temperatures between 30 and 60 °C, along with the corresponding Langmuir and Toth model fits. The experimental results suggest an exothermic behavior of pyrene adsorption on Al-MCM-41, as the adsorptive capacity decreases with increasing temperature. This phenomenon may be attributed to the fact that the interaction between pyrene and the surface of the Al-MCM-41 sample occurs predominantly through Van der Waals forces, characteristic of a physisorption process.

**Fig. 6.** Apparent equilibrium adsorption isotherms of pyrene on Al-MCM-41 in iso-octane solutions at different temperatures (○) 30 °C; (×) 45 °C; (□) 60 °C; (—) Langmuir fit; (- -) Toth fit.



As expected, batch adsorption experiments demonstrated that pyrene retention on the Al-MCM-41 sample is influenced by temperature. The parameters obtained from the Langmuir and Toth equations fittings, along with their correlation coefficients, are shown in Table 4. Both models showed good agreement with the experimental data ( $R^2 > 0.98$ ), indicating that the apparent equilibrium adsorption behavior of pyrene may be described adequately by either equation. In terms of the estimated maximum retention capacity ( $q_m$ ) under each experimental condition, both equations predict higher apparent adsorption equilibrium values at 30 °C (0.912 and 0.804 mmol g<sup>-1</sup> for the Langmuir and the Toth equations, respectively). This difference reflects the different assumptions of each model: while Langmuir considers a uniform adsorption energy distribution, the Toth equation incorporates an assumption of surface heterogeneity. Thus, the higher correlation observed for the fit with the Toth model ( $R^2$  between 0.992 and 0.998), along with the lower estimated values for  $q_m$ , may suggest that the Al-MCM-41 sample may present regions with variable interaction energies between the pyrene molecule and the pores surface, potentially due to the presence of aluminum in its structure.

**Table 4.** Parameters of the Langmuir and Toth equations for pyrene apparent adsorption isotherms in iso-octane solutions.

| Langmuir equation |                               |                               |       | Toth equation                 |                               |       |       |
|-------------------|-------------------------------|-------------------------------|-------|-------------------------------|-------------------------------|-------|-------|
| Temp. (°C)        | $b_L$ (L mmol <sup>-1</sup> ) | $q_m$ (mmol g <sup>-1</sup> ) | $R^2$ | $b_T$ (mmol L <sup>-1</sup> ) | $q_m$ (mmol g <sup>-1</sup> ) | $v$   | $R^2$ |
| 30                | 12.386                        | 0.912                         | 0.985 | $7.9 \cdot 10^{-4}$           | 0.804                         | 5.061 | 0.998 |
| 45                | 9.613                         | 0.874                         | 0.983 | 0.001                         | 0.755                         | 4.850 | 0.995 |
| 60                | 6.934                         | 0.896                         | 0.994 | 0.065                         | 0.781                         | 1.819 | 0.992 |

Therefore, the parameters estimated from both models indicate that pyrene adsorption is governed by the combined effects of interaction intensity and the energetic heterogeneity of

Al-MCM-41, with these influences being more evident at lower temperatures. This outcome supports the use of complementary modeling approaches to describe adsorption equilibrium and highlights the relevance of employing models capable of capturing variations in sites affinity and heterogeneity. Hence, the Al-MCM-41 ability to adsorb pyrene with efficiency, particularly at lower temperatures, underscores its potential as an adsorbent for the removal of PAHs in environmental applications. Optimizing adsorption conditions, such as temperature, may maximize its removal capacity and contribute to the remediation of PAH-contaminated environments.

The heat of adsorption obtained in this study was  $136.1 \text{ kJ mol}^{-1}$ , which is consistent with the order of magnitude reported for MCM-41 systems in previous studies, as summarized in Table 5. The heats of adsorption for naphthalene and anthracene on MCM-41 ( $95.9 \text{ kJ mol}^{-1}$  and  $107.5 \text{ kJ mol}^{-1}$ , respectively) are lower than those observed for pyrene. Furthermore, when comparing the heat of adsorption of Al-MCM-41 with activated carbon, pyrene also showed stronger interaction with the synthesized material, which may be related to the presence of more accessible active sites. Consequently, comparing these results with values obtained in previous studies reveals trends that highlight the effectiveness of the synthesis and modification methods employed in this study. However, variations in adsorption capacity and textural properties should be considered when optimizing Al-MCM-41 for specific applications. The incorporation of aluminum induces the formation of acid sites. In the case of pyrene, a bulky aromatic molecule with  $\pi$  electrons, these acidic sites may act as interaction centers, resulting in a higher adsorption energy than that observed for undoped materials or activated carbon.

**Table 5.** Heats of adsorption for pyrene over Al-MCM-41 and previously reported data for similar systems.

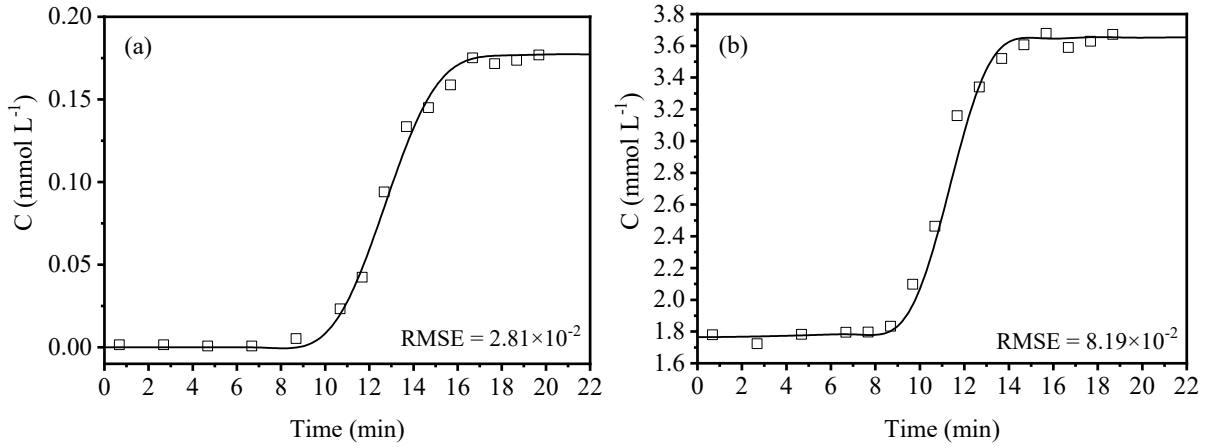
| Adsorbents       | Adsorbate   | $\Delta H$ (kJ mol <sup>-1</sup> ) | Ref.       |
|------------------|-------------|------------------------------------|------------|
| Al-MCM-41        | Pyrene      | 136.1                              | This study |
| MCM-41           | Naphthalene | 95.9                               | [57]       |
| MCM-41           | Anthracene  | 107.5                              | [57]       |
| MCM-41           | Pyrene      | 128.6                              | [57]       |
| Activated Carbon | Pyrene      | 44.9                               | [58]       |

### 3.3 Column adsorption experiments

Experimental and simulated breakthrough curves for two inlet concentrations of pyrene (0.17 and 3.57 mmol L<sup>-1</sup>) are presented in Fig. 7. The low RMSE values obtained for both conditions ( $<8.2 \times 10^{-2}$ ) indicate that the proposed pore and surface diffusion model adequately represents the experimental profiles. For the pyrene inlet concentration of 0.17 mmol L<sup>-1</sup> (Fig. 7a), the pyrene mass-transfer front starts to break at approximately 9–10 min, followed by a gradual increase in concentration until saturation is reached after 20 min. For the pyrene inlet concentration of 3.57 mmol L<sup>-1</sup> (Fig. 7b), the mass-transfer front starts to break at around 8 min, with complete saturation reached at 16 min, approximately 4 min earlier than for the lower pyrene concentration. This narrower transition region reflects a sharper mass-transfer zone, which is expected when higher inlet concentrations impose stronger concentration gradients and increase the rate at which the solid phase approaches equilibrium.

**Fig. 7.** Breakthrough curves of pyrene on the Al-MCM-41 sample at 30°C; (a)  $C_0 = 0.17$  mmol L<sup>-1</sup> (50 mg kg<sup>-1</sup>); (b)  $C_0 = 3.57$  mmol L<sup>-1</sup> (1.000 mg kg<sup>-1</sup>); Flow rate of 0.20 mL min<sup>-1</sup>.

Full lines are the model predictions.



The estimated values for the surface diffusivity coefficients ( $D_s$ ) obtained from the model for several pyrene inlet concentrations (between 0.17 and 3.57 mmol L<sup>-1</sup>) are presented in Table 6. The values for the liquid-phase dispersion ( $D_L$ ), the external film mass-transfer ( $k_f$ ), and the pore diffusivity coefficient ( $D_p$ ) coefficients, calculated using equations 16-18 are also listed in Table 6. A clear concentration dependence is observed for the surface diffusivity, with  $D_s$  increasing as the inlet pyrene concentration ( $C_0$ ) increases. This may be attributed to the higher availability of the pyrene molecules to interact with the Al-MCM-41 surface, thereby enhancing transport along the fluid-solid interface. In addition, the estimated  $D_p$  values are on the order of  $10^{-8}$  cm<sup>2</sup> min<sup>-1</sup>, suggesting that although intraparticle pore diffusion contributes to overall mass transfer, the surface diffusivity becomes the dominant parameter at higher pyrene concentrations. The variation in  $D_s$ , between 9.81 and  $348 \times 10^{-10}$  cm<sup>2</sup> min<sup>-1</sup>, highlights the importance of accounting for surface transport when modeling and predicting adsorption column dynamics. The obtained  $k_f$  and  $D_L$  values are typical of liquid-phase systems operating at low linear velocities, indicating that the external film resistance was not a limiting factor in this system [59].

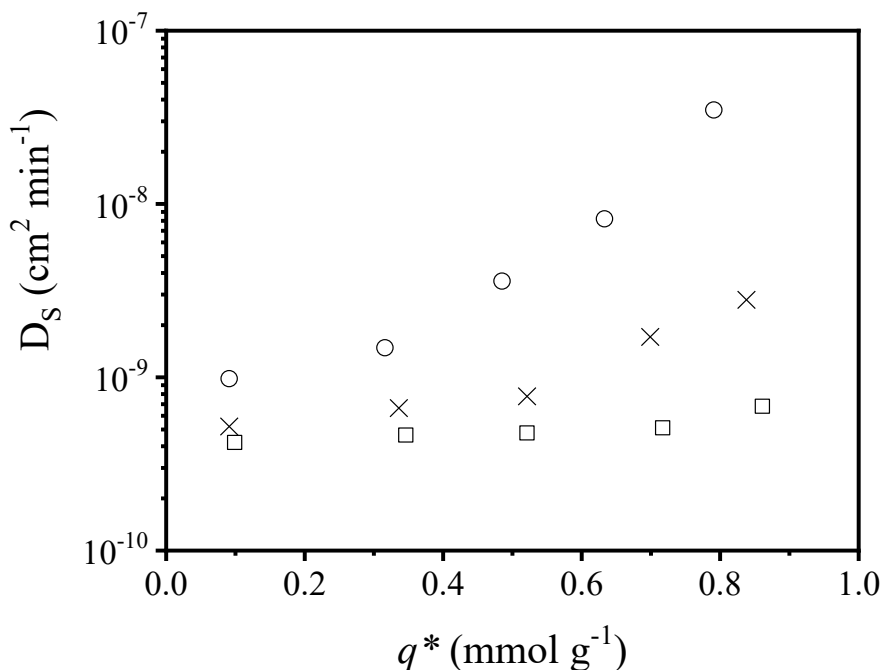
**Table 6.** Estimated mass-transfer parameters for pyrene adsorption on Al-MCM-41 at 30°C, from breakthrough experiments (flow rate of 0.20 ml min<sup>-1</sup>).

| $C_0$ (mmol L <sup>-1</sup> ) | $D_L$ (cm <sup>2</sup> min <sup>-1</sup> ) | $k_f$ (cm min <sup>-1</sup> ) | $D_p$ (cm <sup>2</sup> min <sup>-1</sup> ) | $D_S$ (cm <sup>2</sup> min <sup>-1</sup> ) |
|-------------------------------|--------------------------------------------|-------------------------------|--------------------------------------------|--------------------------------------------|
| 0.17                          |                                            |                               |                                            | $9.81 \times 10^{-10}$                     |
| 0.37                          |                                            |                               |                                            | $1.48 \times 10^{-9}$                      |
| 0.71                          | 2.60                                       | 2.21                          | $3.16 \times 10^{-8}$                      | $3.59 \times 10^{-9}$                      |
| 1.76                          |                                            |                               |                                            | $8.20 \times 10^{-9}$                      |
| 3.57                          |                                            |                               |                                            | $3.48 \times 10^{-8}$                      |

The surface diffusivity values estimated from the model are presented in Fig. 8, as a function of the adsorbed-phase concentrations, along with the values corrected using either the Darken/Langmuir or the Darken/Toth equations (Eq. 21 and 22, respectively). The values obtained directly from the model reveal a progressive increase in  $D_S$  with increasing  $q^*$ , suggesting that the contribution of the surface diffusion coefficient becomes more significant as a larger fraction of the interaction sites on the porous surface is occupied. This trend indicates that the mobility of the adsorbed molecules along the internal surface is influenced by their degree of site occupation.

The application of the Darken correction incorporates the thermodynamic factor associated with changes in the Gibbs free energy of adsorption as surface loading increases. Accordingly, when the correction is applied using the Toth isotherm, the resulting  $D_{S0}$  values exhibit only modest variations across the entire range of  $q^*$ , which is linked to the energetic heterogeneity parameter considered for the Al-MCM-41 surface. Because the Toth equation distributes adsorption affinities over a broader energy spectrum, the corresponding thermodynamic factor varies more gradually with surface coverage, leading to a corrected diffusivity that shows fewer variations as a function of  $q^*$ .

**Fig. 8.** Surface diffusivities for pyrene on Al-MCM-41 at 30°C. (○) Surface diffusivities ( $D_S$ ) estimated from the model; (×) Corrected surface diffusivities ( $D_{S0}$ ) using the Darken/Langmuir equation; (□) Corrected surface diffusivities ( $D_{S0}$ ) using the Darken/Toth equation.



In contrast, the Darken correction based on the Langmuir isotherm results in a sharper increase in  $D_{S0}$  with increasing  $q^*$  when compared to what was observed for the Toth model. This behavior arises from the assumption of energetic homogeneity of the adsorption sites, inherent to the Langmuir model. Under this premise, the thermodynamic factor becomes more sensitive to changes in surface coverage, thereby amplifying the corrected diffusivity as  $q^*$  increases. The comparison between the two corrected trends thus highlights the role of surface heterogeneity in shaping how surface diffusion is influenced by variations in the adsorbed phase concentrations.

These results show that the choice of correction equation significantly affects the estimation of the surface diffusivity, highlighting the importance of evaluating the interaction between the adsorbate and the surface. The comparison these three approaches reveals that, without applying the Darken correction, the surface diffusivity may be overestimated, whereas the use of different isotherms provides distinct adjustments depending on the

distribution of active sites and the affinity of pyrene for the Al-MCM-41 surface. These findings indicate that both the occupation of interaction sites within the porous solid and the underlying energetic distribution of the adsorbent may modulate the interaction of the pyrene molecules along the internal surface.

## 4 Conclusions

The synthesized Al-MCM-41 sample demonstrated potential for removal of PAH compounds in hydrocarbons mixture. Its characterization confirmed the structural and textural attributes expected for an ordered mesoporous aluminosilicate. The surface area ( $540 \text{ m}^2 \text{ g}^{-1}$ ), pore volume ( $0.560 \text{ cm}^3 \text{ g}^{-1}$ ), and particle porosity (0.41) collectively indicate an accessible and hierarchically organized structure. These findings show that the obtained Al-MCM-41 sample provides a favorable porous structure for adsorption and diffusion processes, supporting its application in the investigation of pyrene retention behavior by adsorption. In summary, it combines large mesopores, very high surface area, significant pore volume, and surface acidity, enabling efficient adsorption of bulky aromatic molecules that cannot readily access conventional microporous adsorbents.

The batch adsorption experiments demonstrated that the pyrene retention on the Al-MCM-41 sample is influenced by temperature, confirming predominant physisorption behavior. The equilibrium data were well represented by the Langmuir and Toth fitting equations ( $R^2 > 0.98$ ). The heterogeneity accounted for in the Toth model is consistent with the incorporation of aluminum into the structure, which modifies the distribution of the adsorption sites. The estimated heat of adsorption ( $136.1 \text{ kJ mol}^{-1}$ ) is in good agreement with previously reported values for MCM-41.

The phenomenological model, based on pore and surface diffusion, adequately reproduced the breakthrough curves. The estimated parameters indicate that mass transfer is

represented by the coupled contribution of these mechanisms. At low concentrations, pore diffusion ( $D_p$ ) coefficient is more relevant, with values approximately two orders of magnitude higher than surface diffusion ( $D_s$ ). However, increasing the concentration, the  $D_s$  values also increased and reached the same order of magnitude as  $D_p$ . Furthermore, the comparison of diffusivities corrected using the Darken method reinforces that surface heterogeneity may modulate the relationship between the adsorbed phase concentration and the molecular transport at the fluid-solid interface. Thus, through the integrated experimental–computational approach, it was possible to highlight the potential of Al-MCM-41 as an adsorbent for PAH removal, as well as to establish important insights into the adsorption and diffusion transport phenomena.

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## Author contributions

Rafael T. Landim: Conceptualization, Methodology, Investigation, Formal analysis, Validation, Data curation, Visualization, Writing – original draft; Solange A. Quintella: Investigation, Validation, Data curation, Writing – review and editing; Antônio S. Araújo: Validation, Supervision, Writing – review and editing; Joaquin Silvestre-Albero: Validation, Supervision, Writing – review and editing; Célio L. Cavalcante Jr.: Funding acquisition, Resources, Supervision, Project administration, Writing – review & editing; F. Murilo T. Luna: Conceptualization, Methodology, Supervision, Funding acquisition, Project administration, Writing – review & editing.

|    |                |                                                                              |
|----|----------------|------------------------------------------------------------------------------|
| 1  | <b>Symbols</b> |                                                                              |
| 2  | $b_L$          | Langmuir equation parameter ( $\text{L mmol}^{-1}$ )                         |
| 3  | $b_T$          | Toth equation parameter ( $\text{L mmol}^{-1}$ )                             |
| 4  | $C$            | Bulk liquid phase concentration ( $\text{mmol L}^{-1}$ )                     |
| 5  | $C_p$          | Intra-particle liquid phase concentration ( $\text{mmol L}^{-1}$ )           |
| 6  | $C_0$          | Initial concentration ( $\text{mmol L}^{-1}$ )                               |
| 7  | $C_e$          | Equilibrium concentration ( $\text{mmol L}^{-1}$ )                           |
| 8  | $d_p$          | Average particle diameter (cm)                                               |
| 9  | $D$            | Column diameter (cm)                                                         |
| 10 | $D_m$          | Molecular diffusion coefficient ( $\text{cm}^2 \text{min}^{-1}$ )            |
| 11 | $D_p$          | Pore diffusion coefficient ( $\text{cm}^2 \text{min}^{-1}$ )                 |
| 12 | $D_{p0}$       | Corrected pore diffusion coefficient ( $\text{cm}^2 \text{min}^{-1}$ )       |
| 13 | $D_L$          | Axial dispersion coefficient ( $\text{cm}^2 \text{min}^{-1}$ )               |
| 14 | $k_f$          | Film mass transfer coefficient ( $\text{cm min}^{-1}$ )                      |
| 15 | $K$            | Adsorption constant in the Henry's Law region ( $\text{L g}^{-1}$ )          |
| 16 | $L$            | Column length (cm)                                                           |
| 17 | $M$            | Molecular weight                                                             |
| 18 | $M_A$          | Mass of adsorbent (g)                                                        |
| 19 | $n$            | Step sequence                                                                |
| 20 | $Q$            | Flow-rate ( $\text{mL min}^{-1}$ )                                           |
| 21 | $q$            | Solid phase concentration ( $\text{mmol g}^{-1}$ )                           |
| 22 | $q^*$          | Solid phase concentration in equilibrium with $C_p$ ( $\text{mmol g}^{-1}$ ) |
| 23 | $q_m$          | Langmuir equation parameter, saturation capacity ( $\text{mmol g}^{-1}$ )    |
| 24 | $r$            | Radial coordinate                                                            |
| 25 | $R$            | Universal gas constant ( $\text{kJ mol}^{-1} \text{K}^{-1}$ )                |

|    |                      |                                                                            |
|----|----------------------|----------------------------------------------------------------------------|
| 1  | $R_p$                | Particle radius (cm)                                                       |
| 2  | $Re$                 | Dimensionless Reynolds number                                              |
| 3  | $Sh$                 | Dimensionless Sherwood number                                              |
| 4  | $Sc$                 | Dimensionless Schmidt number                                               |
| 5  | $t$                  | Time (min)                                                                 |
| 6  | $T$                  | Absolute temperature (K)                                                   |
| 7  | $u$                  | Superficial velocity (cm min <sup>-1</sup> )                               |
| 8  | $V_b$                | Molar volume at normal boiling point (cm <sup>3</sup> gmol <sup>-1</sup> ) |
| 9  | $V_s$                | Volume of the solution (L)                                                 |
| 10 | $z$                  | Axial coordinate                                                           |
| 11 |                      |                                                                            |
| 12 | <b>Greek symbols</b> |                                                                            |
| 13 | $\varepsilon$        | Bed porosity                                                               |
| 14 | $\varepsilon_p$      | Particle void fraction                                                     |
| 15 | $\rho_{ap}$          | Particle apparent density (g cm <sup>-3</sup> )                            |
| 16 | $\Delta H_{ads}$     | Adsorption enthalpy (kJ mol <sup>-1</sup> )                                |
| 17 | $\Delta H_{sol}$     | Solvent adsorption enthalpy (kJ mol <sup>-1</sup> )                        |
| 18 | $\Delta U_{ap}$      | Apparent heat of adsorption (kJ mol <sup>-1</sup> )                        |
| 19 | $\phi$               | Association coefficient                                                    |
| 20 | $\eta$               | Viscosity of the solution (cP)                                             |
| 21 | $v$                  | Parameter related to the degree of heterogeneity of the adsorbent surface  |

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