Assessing Mass Transfer Coefficients in Porous Adsorbents: Microcalorimetry *vs.* Uptake

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Abstract

Mass transfer parameters are crucial for the assessment of adsorption kinetics and the design of adsorption processes. In this work, CO_2 adsorption at 298 K was investigated by two approaches: one based on microcalorimetric data and the other using gravimetric uptake experiments. Both models include mass and energy balances, involving a set of partial equations that must be solved simultaneously, with the mass transfer being described by the Linear Drive Force (LDF) approximation. A microporous and a mesoporous material were tested to verify the suitability of the approaches to different pore structures. Each methodology was tested across a few pressure steps, to compare the sensibility. It is possible to observe homogeneity in the obtained data, which fluctuated in the same order of magnitude. This shows a good agreement between the two methods when compared to each other, indicating good experimental and mathematical consistency of both methods.

Keywords: Adsorption kinetics; Microcalorimetry; Uptake fitting; LTA zeolite; Activated alumina.

1. Introduction

The assessment of adsorption kinetics can be conducted using various techniques that enable the precise handling of adsorption uptake data in a well-controlled environment [1, 2].

The main objective of this study is to estimate the mass transfer coefficient using two different approaches: microcalorimetric analysis and uptake experiments. In both methods, a series of mass and energy balances are applied to describe the systems and fit the adsorption kinetics parameters.

2. Materials and methods

2.1 Materials

Carbon dioxide was employed as a probe molecule in two different types of adsorbents: a commercial LTA zeolite and activated alumina. Both materials were shaped into pellets.

2.2 Experimental

Textural characterization was carried out by measuring nitrogen and carbon dioxide adsorption/desorption isotherms at 77 and 273 K, respectively, with an Autosorb-iQ3 instrument (Quantachrome, USA). Apparent surface areas were estimated by the BET method, the average pore size was obtained by BJH method and the micropore volumes were calculated by the Dubinin-Radushkevich equation.

The uptake of CO_2 at 298 K was obtained with a magnetic suspension balance equipped with a gas dosing unit (Rubotherm, Germany). The adsorption heat was measured using a Tian-Calvet microcalorimeter (Setaram model C80, France).

Before each experiment, the samples were degassed under vacuum: the LTA at 573 K for 10 hours and alumina at 473 K for 6 hours.

2.1 Modeling

The mass transfer of the component *i* within an adsorbent particle was described by a set of equations comprising the mass balance for the adsorbed and bulk phases. Given the exothermic nature of the adsorption process, the heat effects must also be taken into account [1].

The mass diffusion was simplified by the use of the Linear Driver Force approach introduced by Glueckauf and Coates (1947) [3]. According to this model, the rate of adsorption uptake is proportional to the difference between the concentration at the particle surface (equilibrium adsorbed amount) and the average concentration within the particle (volume-average adsorption amount) [1, 3]. This

relationship is expressed by Eq. 1.

$$\frac{\partial \bar{q}}{\partial t} = k_{LDF}(q_e - \bar{q}) \qquad (1)$$

where the k_{LDF} is the effective linear driver force coefficient.

The mathematical model was developed according to the applied experimental method. The microcalorimetric method is based on the study of Richard et al. (2021), that proposed a mass and energy balance system to describe mass transfer resistance from calorimetric peaks obtained in a Tian-Calvet microcalorimeter [2]. The uptake method consists of applying the LDF approach to describe the uptake obtained in the gravimetric system operating under isothermal conditions [4, 5]. Table 1 lists the main parameters used in both models.

Table 1. Parameters used in both methods.

Properties	Values	Ref
Heat capacity of CO_2 at 298 K ($J\ mol^{-1}K^{-1}$)	37.6	[6]
Heat capacity of LTA at 298 K ($J\ kg^{-1}\ K^{-1}$)	938.0	[4]
Heat capacity of alumina at 298 K ($J\ kg^{-1}\ K^{-1}$)	811.3	[7]
Density of LTA ($kg\ m^{-3}$)	704.0	[4]
Density of alumina ($kg\ m^{-3}$)	769.0	[8]
LTA/CO_2 av. ads. enthalpy ($kJ\ mol^{-1}$)	-61.89	[a]
Alumina/CO_2 av. ads. enthalpy ($kJ\ mol^{-1}$)	-41.28	[a]

[a] Obtained experimentally

3. Results and discussion

Textural Characterization

Fig. 1 (a) shows the N_2 adsorption/desorption isotherm at 77 K for the LTA and alumina samples. The isotherm for alumina presents a type II shape, indicating the presence of larger pores in its structure. Besides, a H4 loop type hysteresis is observed, which was associated with the pore filling mechanism [9]. In contrast, the LTA zeolite has a kinetic restriction for the N_2 molecules at cryogenic temperatures, as indicated by its low adsorption capacity [4]. Fig. 1 (b) shows the CO_2 adsorption isotherms at 273 K. The LTA sample exhibits a higher CO_2 adsorption capacity compared to alumina, which is attributed to its significant microporosity.
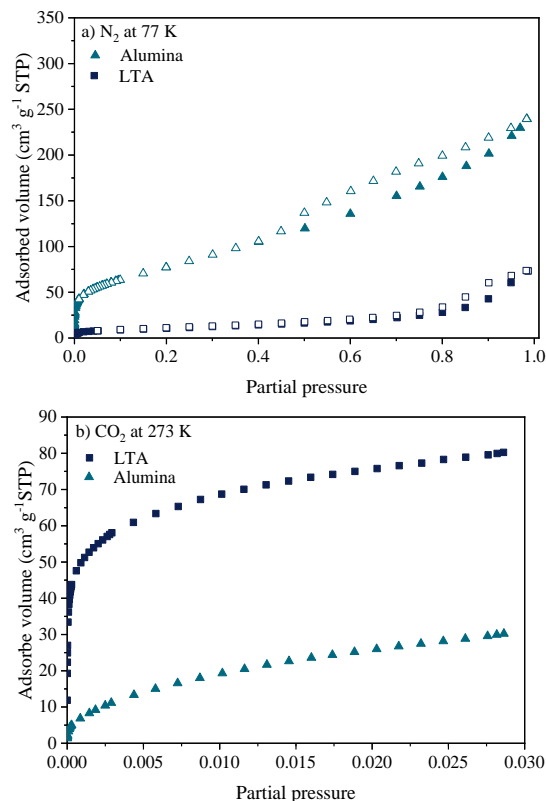

Fig. 1. Adsorption/desorption isotherms for (a) N_2 at 77 K and (b) CO_2 at 273 K.

Table 2 summarizes the textural characteristics obtained from the adsorption isotherms in Fig. 1 for the studied samples.

Table 2. Textural characterization data.

Sample	BET area (m^2g^{-1})	Pore size (nm)	N_2 DR-volume (cm^3g^{-1})	CO_2 DR-volume (cm^3g^{-1})
LTA[a]	39	0.4	0.010	0.180
Alumina	284	3.83[b]	0.092	0.047

[a] Nascimento B.O. *et al.* [4] and [b] BJH method.

CO_2 isotherms and uptakes

Fig. 2 shows the CO_2 adsorption isotherm at 298 K for the samples. The higher adsorption capacity of the zeolite is again observed. The indicated equilibrium points provided the uptake curves used in the model simulations.
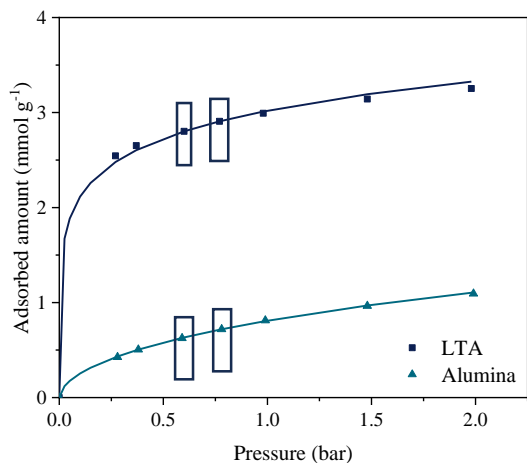
Fig. 2. CO_2 adsorption isotherms at 298 K. Symbols are experimental data and lines represent the fit by Sips model [5].

Fig. 3 presents the gravimetric CO_2 adsorption uptake, both experimental and simulated data, for the LTA and alumina samples. The model (lines) shows a good agreement with the experimental data.
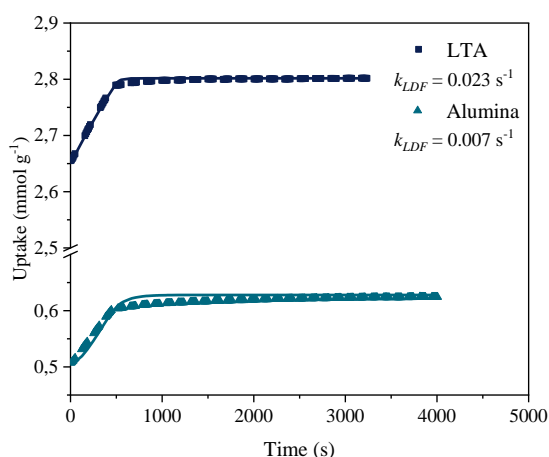

Fig. 3. CO_2 adsorption uptakes for LTA and alumina at the pressure of 0.60 bar. Symbols are experimental data and lines denote the fit by the model [2].

Table 3 presents LDF coefficients obtained using the adsorption uptake model adjusted for LTA and alumina. CO_2 mass transfer parameters are of the same order of magnitude as those achieved by the microcalorimetric method. For the LTA sample, these data corroborate the results reported in the literature [10].

Table 3. Mass transfer constants obtained by the uptake method at different pressures.

LTA		Alumina	
Equilibrium pressure (bar)	k_{LDF} (s^{-1})	Equilibrium pressure (bar)	k_{LDF} (s^{-1})
0.60	0.023	0.59	0.007
0.77	0.019	0.78	0.006

Adsorption Enthalpy and microcalorimetric peaks

Fig. 4 shows the adsorption enthalpy as a function of the adsorbed amount of CO_2 at 298 K. Both materials exhibit characteristics of heterogeneous interactions between adsorbate and adsorbent. This behavior could be associated with the surface chemistry (e.g. presence of cations) and the pore size distribution. In the case of alumina, as a material has a large pore size, a rapid decrease in adsorption enthalpy values can be observed, while the zeolite sample present a gradual decrease [11].
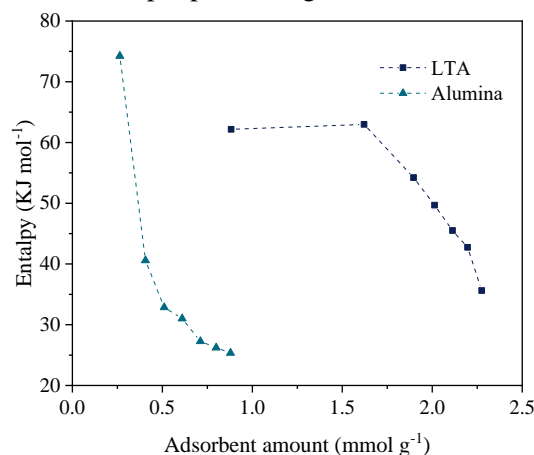

Fig. 4. CO_2 adsorption enthalpy curves for LTA and alumina samples at 298 K.

Fig. 5 presents the experimental microcalorimetric peaks for the studied samples. In both cases, the heat transfer coefficients were estimated based on blank expansion experiments [2]. In the figure, within approximate the same pressure range, the LTA sample releases more energy than alumina, which agrees to the Fig. 4, where the average adsorption enthalpy of the zeolite is higher than that of alumina.
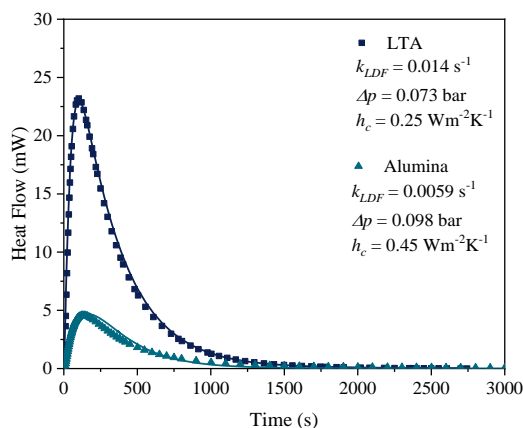
Fig. 5. Experimental (symbols) and calculated (lines) calorimetric peaks for LTA and alumina. Lines represent the fit by the model.

Table 4 summarizes the mass transfer parameters obtained by microcalorimetry.

Table 4. Mass transfer constants obtained by the microcalorimetric method at different pressures.

LTA		Alumina	
Equilibrium pressure (bar)	k_{LDF} (s^{-1})	Equilibrium pressure (bar)	k_{LDF} (s^{-1})
0.44	0.014	0.33	0.006
0.53	0.018	0.43	0.009
0.61	0.028	0.61	0.009

Both materials require nearly the same time to reach equilibrium (see Fig. 4). However, the LTA zeolite exhibits a steeper isotherm and a higher uptake capacity compared to alumina under similar pressure and temperature conditions. As a result, the concentration gradient for the same pressure step is greater in the zeolite than in the alumina, which leads to a steeper concentration front within the bed. Therefore, the LDF coefficient, as a lumped fitting parameter, might be reflecting the more rectangular isotherm of the zeolite, leading to higher k_{LDF} values for the zeolite. Despite this, a good agreement can be observed between both methods of mass transfer assessment.

4. Conclusions

In this work, two models were used to estimate the effective linear driver force coefficient (k_{LDF}) for CO_2 adsorption in two different materials. In both cases, the calculated results were consistent and comparable to literature, indicating a high degree of experimental and mathematical agreement between the methods.

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