Chemical Engineering Journal 161 (2010) 173–181

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Modeling CO_2 adsorption on amine-functionalized mesoporous silica: 1. A semi-empirical equilibrium model

Rodrigo Serna-Guerrero[a], Youssef Belmabkhout[b], Abdelhamid Sayari[a,b,*]

[a] Department of Chemical and Biological Engineering, University of Ottawa, 161 Louis Pasteur, Ottawa, ON K1N 6N5, Canada
[b] Department of Chemistry, University of Ottawa, 10 Marie Curie, Ottawa, ON K1N 6N5, Canada

ARTICLE INFO

Article history:
Received 16 February 2010
Received in revised form 10 April 2010
Accepted 12 April 2010

Keywords:
CO_2 adsorption
MCM-41
Aminosilane grafting
Adsorption isotherm
Heat of adsorption

ABSTRACT

An equilibrium model capable of describing CO_2 adsorption isotherms on amine-grafted mesoporous silica using a semi-empirical method was developed. The proposed model is based on the assumption that adsorption of CO_2 occurs via two independent mechanisms: (i) chemical adsorption on the amine-functional groups, and (ii) physisorption on the surface of the adsorbent. The CO_2 adsorption isotherms on triamine-grafted pore-expanded MCM-41 silica were measured at different temperatures and used to develop the proposed model. The equilibrium model was capable of describing CO_2 adsorption over a wide range of pressure, from 0.001 to 20 bar. Furthermore, when applied in a temperature-dependent form, it fitted experimental data at different temperatures between 25 and 55 °C. The adequacy of the model was reflected by the low values of the normalized standard deviations (<8%) obtained at all temperatures. The model was also successfully used to fit experimental CO_2 isotherms of a triamine-grafted mesoporous silica with lower amine content and five varieties of monoamine-grafted SBA-15, as well as experimental data for H_2S adsorption at 25, 35 and 50 °C. Moreover, the heat of CO_2 and H_2S adsorption calculated using the temperature-dependent parameters of the proposed model was in excellent agreement with experimental data.

1. Introduction

As we enter the second decade in this new millennium, it has become evident that one of the major challenges faced by our generation is the reduction of contaminant emissions to the environment despite industrialization's unstoppable progress. The release of carbon dioxide (CO_2) poses a particular predicament: a product of the large consumption of fossil fuels, CO_2 is considered as a major anthropogenic contribution to climate change. As a result, various methods to capture CO_2 in an efficient, cost-effective manner are currently under study. Among those alternatives, the technology considered nowadays as mature is CO_2 scrubbing using amine solutions. Unfortunately, several concerns are associated with liquid amine absorption, including high energy requirements for solvent regeneration, extensive corrosion of the equipment [1,2] and, recently, the impact of the amine solutions life cycle on the surrounding ecosystems [3]. Thus, several adsorption separation technologies are actively pursued to develop a competitive, lower cost alternative.

Currently, vast efforts by the scientific community are underway to produce suitable adsorbents capable of handling the operating demands of CO_2 emitting sources, ranging from new approaches using well known adsorbents like zeolites [4,5] and activated carbons [6,7] to the exploration of new materials such as periodic mesoporous silicas [8–19] and metal organic frameworks (MOFs) [20–23]. Inspired by the current liquid amine CO_2 scrubbing technology, amine groups have been incorporated onto a number of solid supports for the removal of carbon dioxide (CO_2) from gaseous mixtures [8–20]. The objective of such effort was to exploit the efficient amine–CO_2 interactions, while preventing the aforementioned shortcomings of the liquid–gas systems. In particular, a variety of amine-bearing molecules have been incorporated into periodic mesoporous silicas (for a review, see Harlick and Sayari [24] and Choi et al. [25]). Due to their suitable structural characteristics, ordered mesoporous materials drew, in recent years, the attention of researchers in many fields, particularly in catalysis and adsorption. Typically, this class of materials exhibits large surface area and pore volume with narrow pore size distribution in the nanometer range [26,27]. Furthermore, the possibility to tailor their pore systems, including pore size, volume and connectivity [28–30] and to incorporate surface and/or framework functional groups [31,32] makes them versatile materials that can be exploited for a wide range of applications. As far as amine-functionalized mesoporous silicas are concerned, it has been found that (i) up to a certain amine content, the CO_2 adsorption capacity increases with the content of functional groups attached on the surface, and (ii) only when

---

* Corresponding author.
E-mail address: abdel.sayari@uottawa.ca (A. Sayari).

1385-8947/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2010.04.024

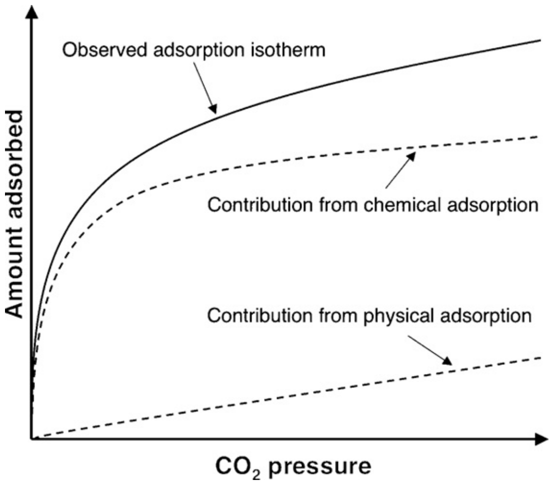

Fig. 1. Schematic representation of CO_2 adsorption on amine-functionalized mesoporous adsorbents.

the adsorbent maintains an open pore structure are the amines efficiently used, especially when adsorption occurs at temperatures close to ambient [33].

Because, in general, amine-functionalized mesoporous materials have proven to be promising in terms of adsorption capacity, kinetics and stability in some cases, it was deemed attractive to model the behavior of such systems for its subsequent simulation and interpretation. However, based on our own data [17,33] and on the literature reports [8,14,15,19], it was observed that for properly synthesized amine-functional mesoporous materials, the CO_2 adsorption isotherms exhibit an unusual shape, as represented schematically in Fig. 1. Unlike a typical Langmuir isotherm, consistent with chemical adsorption, CO_2 adsorption isotherms for amine-functionalized mesoporous adsorbents do not exhibit a saturation plateau at high pressure. As shown in Fig. 1, after a dramatic uptake of CO_2 at low concentration, the adsorption capacity kept increasing with the partial pressure of the adsorbate. Accordingly, the common isotherm models (e.g. Langmuir, Freundlich) seem adequate to describe the adsorption profile only within a small range of concentration, particularly at low CO_2 pressure. A plausible explanation to this shape is the occurrence of a second independent mechanism for CO_2 adsorption, in addition to the CO_2 capture by amine groups. In a previous contribution [33], it was suggested that the overall adsorption of CO_2 on amine-functionalized mesoporous silicas is the result of both chemical interactions with the amine groups and physisorption on the surface of the adsorbent. Since then, other authors exploring CO_2 capture on functionalized adsorbents have adopted this hypothesis as well [5]. It has also been observed that the purely siliceous support had a small capacity for CO_2 at low partial pressure due to physical adsorption but, as the pressure of CO_2 increased, its uptake became significant [34,35].

To the best of our knowledge, the shape of the CO_2 adsorption isotherm over amine-functionalized mesoporous materials has not been analyzed in depth before, nor fit to an appropriate isotherm model. Thus, in the first part of this series, a semi-empirical model to fit the CO_2 adsorption data on amine-functionalized mesoporous materials over a wide range of pressure and temperature is proposed. Because the adsorption of CO_2 on amine-grafted mesoporous materials can be a result of complex interaction mechanisms [33], our objective was to develop a model with a wide scope using characterization data routinely produced and a series of justifiable assumptions. Earlier, our group developed a material with characteristics suitable for the incorporation of large amounts of surface organic species [29]. This material, referred to as PE-MCM-41, consisted of a mesoporous silica type MCM-41 whose pores have been enlarged by a post-synthesis hydrothermal expansion. PE-MCM-41 exhibited a readily accessible pore structure even after surface amine functionalization [24,33], making it suitable for generating high-quality CO_2 adsorption isotherms.

1.1. Description of the proposed equilibrium model

The model considers a simultaneous uptake of adsorbate by physical and chemical interactions, thus consisting of the sum of two independent adsorption mechanisms, as expressed by Eq. (1):

$$q = q_{chem} + q_{phys} \tag{1}$$

where q is the total adsorption uptake, q_{chem} is the CO_2 uptake by amine groups and q_{phys} represents the CO_2 uptake by physisorption on the adsorbent surface. A dual-site model of this form assumes no interaction between the species adsorbed on each of the two types of adsorption sites. Such an assumption has been generally accepted when there are large differences between the adsorption energy of each type of site, resulting in a distinct preferential adsorption on one of them at low surface coverage [36]. Indeed, this appears to be the case of CO_2 adsorption on amine-functional silica based on the observations that (i) amine functionalization enhances the adsorption capacity particularly at low concentrations [20,33] and (ii) the measurements of heat of adsorption by calorimetry consistently reported high values associated to chemisorption at low surface coverage and approaching those of physisorption on pure silica at higher CO_2 loading [10,13,39].

The right-hand side terms of Eq. (1) can be represented using existing isotherm models with independent coefficients for each adsorption mechanism. In this work, we propose to use the Toth isotherm model to represent each of the adsorption mechanisms since it has a temperature-dependent form that makes it useful for modeling not only isothermal but also non-isothermal behavior [34,36]. In addition, the Toth isotherm has a coefficient associated with the isosteric heat of adsorption at zero coverage (ΔH), which can provide further physical meaning to the proposed model.

Thus, the model can be represented as:

$$q = \left[\frac{n_s bP}{\left(1+(bP)^t\right)^{1/t}}\right]_{chem} + \left[\frac{n_s bP}{\left(1+(bP)^t\right)^{1/t}}\right]_{phys} \tag{2}$$

where P is the pressure of the adsorbate, n_s, b and t are the characteristic parameters of the Toth model, and the subscripts "*chem*" and "*phys*" denote the contribution from each of the mechanisms to the overall adsorption capacity. To express the Toth isotherm as a function of temperature, the model coefficients are represented in the form of Eqs. (3)–(5):

$$b = b_0 \exp\left[\frac{\Delta H}{RT_0}\left(\frac{T_0}{T} - 1\right)\right] \tag{3}$$

$$t = t_0 + \alpha\left(1 - \frac{T_0}{T}\right) \tag{4}$$

$$n_s = n_{s0} \exp\left[\chi\left(1 - \frac{T}{T_0}\right)\right] \tag{5}$$

where ΔH is the heat of adsorption at a surface coverage close to zero, R is the universal gas constant, α and χ are the parameters of the temperature-dependent form of the Toth model and the subscript 0 refers to the parameters obtained under a reference temperature T_0.

The main challenge in the implementation of this model is to discriminate between the contributions of each adsorption mechanism in the overall CO_2 uptake measured experimentally. Thus, a proposed method is to calculate q_{phys} based on the adsorption data of CO_2 on the siliceous support before functionalization under the assumption that physical adsorption does not depend strongly on

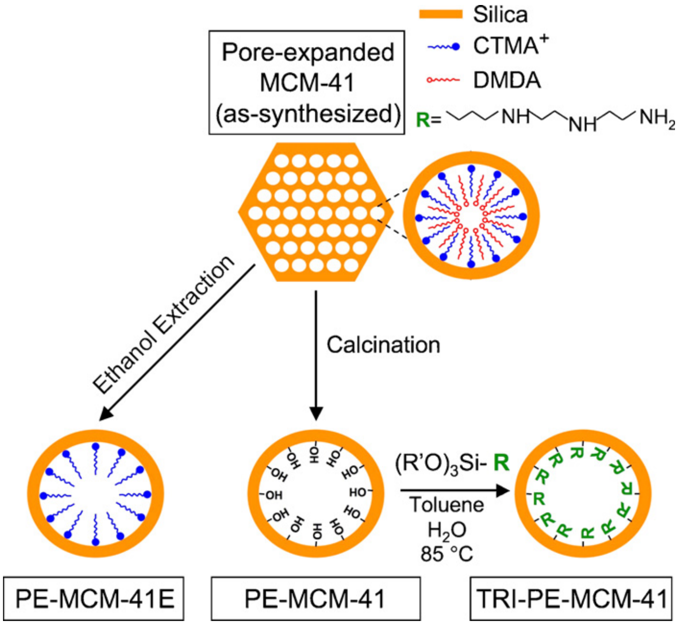

Fig. 2. Schematic representation of the synthesis of mesoporous adsorbents.

the nature of the surface whether it is the siliceous support or its functionalized counterpart. Due to the weak interactions involved in physisorption, this is a reasonable assumption. Nonetheless, further support to this supposition will be provided later in this work. Thus, as long as capillary condensation does not occur and the inner surface of the material is freely accessible, the CO_2 uptake by physical adsorption can be considered proportional to the surface area. Under such assumption, the amount of CO_2 physisorbed on the surface of the functionalized adsorbent at any given CO_2 pressure is related to the CO_2 uptake by the unmodified silica support under the same pressure and temperature conditions according to Eq. (6):

$$q_{phys@P/P0} = q_{\mathrm{support}@P/P0}\frac{S}{S_{\mathrm{support}}} \tag{6}$$

where q_{support} and S_{support} are the CO_2 uptake and surface area of the purely siliceous mesoporous support, respectively, and S is the surface area of the amine-containing adsorbent.

Once the contribution from physical adsorption is established, it can be subtracted from the total CO_2 uptake to calculate the amount adsorbed due to the chemical interaction between CO_2 and amines. In this manner, the contribution from the amine groups (q_{chem}) can be fitted to an appropriate isotherm model and, when added to q_{phys}, will describe the overall CO_2 uptake due to the combined contributions of the two independent mechanisms.

To estimate the accuracy of the fit of the proposed model, an error function based on the normalized standard deviation was calculated as follows:

$$\Delta q(\%) = \sqrt{\frac{\sum[(q_{\mathrm{exp}} - q_{\mathrm{mod}})/q_{\mathrm{exp}}]^2}{N-1}} \tag{7}$$

where $\Delta q(\%)$ is the normalized standard deviation, q_{exp} and q_{mod} are the experimental and calculated amounts of CO_2 adsorbed, and N is the number of data points available in each isotherm.

2. Experimental

2.1. Synthesis of the adsorbent

The synthesis of the mesoporous adsorbent has been described in detail elsewhere and is represented in Fig. 2 [24]. Briefly, MCM-41 silica was produced using cetyltrimethylammonium bromide ($CTMA^+Br^-$) as structure directing agent in basic conditions at 100 °C. The post-synthesis pore expansion procedure was performed at 120 °C for 3 days using dimethyldecylamine (DMDA) as expander agent. A sample of this material was calcined under nitrogen, then air at 550 °C for 5 h to obtain PE-MCM-41C (Fig. 2). The amine groups were incorporated by grafting 2-[2-(3-trimethoxysilylpropylamino)ethylamino]ethylamine (TRI-silane) onto the silica surface as follows. PE-MCM-41C was suspended in 150 ml of toluene in a glass vessel, followed by the addition of 0.3 ml of distilled, deionized water per gram of silica. After homogenization of the mixture, the temperature in the reactor was increased to 85 °C and 3 g of TRI-silane per gram of silica was added under vigorous stirring. The reaction proceeded for 16 h. The solid phase was then filtered and washed thoroughly with toluene, then pentane. Finally, the solid was dried in a natural convection oven at 100 °C for 1 h and the product was labeled TRI-PE-MCM-41. An adsorbent with lower amine loading, designated as TRI-PE-MCM-41(dry), was produced by grafting TRI-silane on PE-MCM-41C following the same procedure as described above, but without addition of water. Another material that will be considered in the upcoming discussion is PE-MCM-41E, where "E" stands for "extracted" (Fig. 2). This material consisted of a cetyltrimethylammonium-bearing mesoporous silica produced by the selective extraction of the expander agent with ethanol [37].

2.2. Characterization of the adsorbent

The structural properties of PE-MCM-41C, PE-MCM-41E, TRI-PE-MCM-41 and TRI-PE-MCM-41(dry) were determined by nitrogen adsorption measurements at 77 K using a Micromeritics ASAP 2020 volumetric apparatus. The samples were degassed under vacuum at 150 °C for 5 h before adsorption measurements. The surface area was calculated using the BET method, while the pore volume was considered as the volume of liquid nitrogen adsorbed at a relative pressure close to 1. The pore size distribution was obtained using the KJS method [38]. The organic content was determined by thermogravimeric analysis (TGA) using a TA Q-500 instrument, considering that only the weight lost beyond 200 °C is associated with the decomposition of covalently tethered amine-containing groups [24].

2.3. Adsorption measurements

Measurements of CO_2 adsorption at equilibrium on PE-MCM-41C, PE-MCM-41E, TRI-PE-MCM-41 and TRI-PE-MCM-41(dry) were performed on a Rubotherm microbalance with automated gas dosing system. This system allows the flow of gases at controlled pressures ranging from 0.001 to 60 bar at ambient temperature. In the current work, the adsorbent was pretreated under a flow of 50 ml min^{-1} ultra-high purity nitrogen at 150 °C for 2 h. The sample was subsequently cooled down to the desired temperature (i.e., 25, 35, 45 or 55 °C) before exposure to flowing CO_2 at the desired partial pressure. A minimum equilibration time of 2 h was used for each data point of the isotherm. After this time, the observed weight of the sample remained constant, inferring that equilibrium has been reached. The adsorption capacity was calculated from the weight change of the sample in the presence of CO_2 after accounting for the effect of buoyancy [34]. For each adsorption isotherm, a fresh sample was used. This procedure was also applied to measure the adsorption isotherms of H_2S on TRI-PE-MCM-41 and PE-MCM-41C at 25, 35 and 55 °C. Adsorption data at different temperatures allowed the calculation of the isosteric heat of adsorption (ΔH_{ISO}) using the Clausius–Clapeyron equation. The Toth isotherm param-

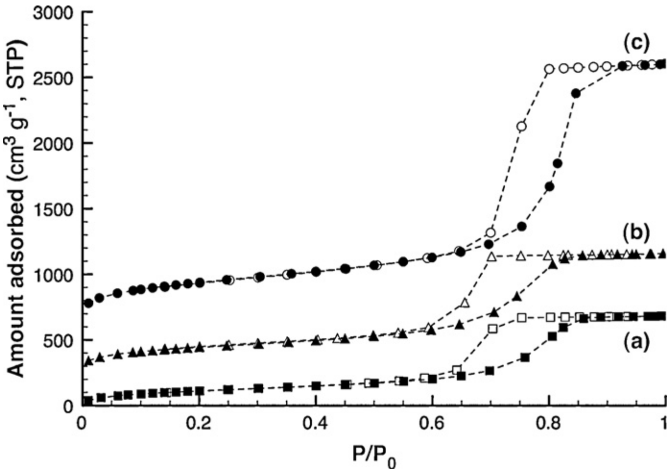

Fig. 3. Nitrogen adsorption (closed symbols) and desorption (open symbols) isotherms for (a) TRI-PE-MCM-41, (b) PE-MCM-41E and (c) PE-MCM-41C. For clarity, isotherms (b) and (c) were shifted upward by 300 and 600 cm^3 g^{-1}, respectively.

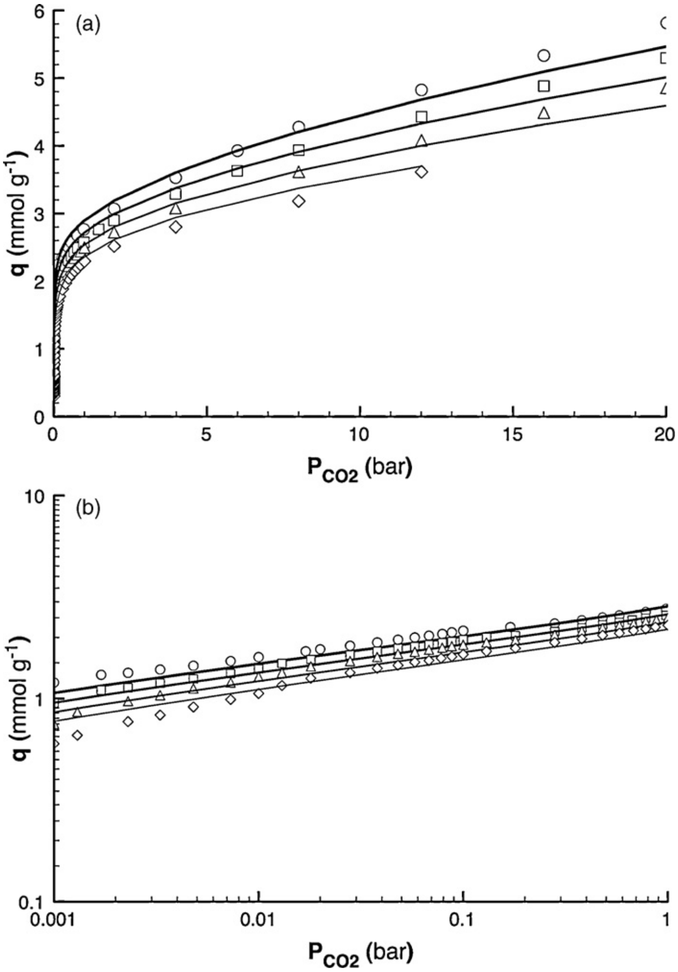

Fig. 4. Adsorption isotherm of CO_2 on TRI-PE-MCM-41 in the (a) high and (b) low pressure range at 25 °C (circles), 35° C (squares), 45 °C (triangles) and 55 °C (diamonds). The solid lines correspond to the equilibrium model proposed in this work.

eters for q_{phys} and q_{chem} were obtained by non-linear regression using an iterative method with the aid of Microsoft Excel©software.

3. Results and discussion

The nitrogen adsorption isotherms obtained for PE-MCM-41C, PE-MCM-41E and TRI-PE-MCM-41 are presented in Fig. 3. The calculated structural properties are shown in Table 1. As can be seen, all samples exhibited a Type IV isotherm according to the IUPAC classification, characteristic of materials with mesoporous structure. After functionalization, smaller pore volume and surface area were observed, attributed to the occurrence of the organic molecules onto the channels' surface. The loading of amine species on the adsorbent was estimated as 7.27 mmol g^{-1} for TRI-PE-MCM-41 and 4.90 mmol g^{-1} for TRI-PE-MCM-41(dry). The surface area of TRI-PE-MCM-41 was of 429 m^2 g^{-1} and 539 m^2 g^{-1} for TRI-PE-MCM-41(dry), which represent 38 and 48% of the surface area of the purely siliceous support, respectively. The amount of organic species (i.e., CTMA$^+$) in PE-MCM-41E, measured by TGA was 1.13 mmol g^{-1}.

With respect to CO_2 adsorption on TRI-PE-MCM-41, Fig. 4 shows the isotherms determined experimentally at different temperatures. All experimental data for CO_2 adsorption on TRI-PE-MCM-41 were included in the Supporting Information section, Table S1. The shape of these isotherms is in agreement with other isotherms reported in the literature [8,14,15,17,19,33]. Indeed, a steep uptake of CO_2 was observed at low CO_2 partial pressures followed by a small, but steady increase at high pressure.

Fig. 5 shows the adsorption isotherms of CO_2 on PE-MCM-41C at different temperatures. Tabulated experimental data are available in the Supporting Information section, Table S2. Within the range of pressures analyzed, there was no capillary condensation of CO_2. It should also be mentioned that the CO_2 uptake on PE-MCM-41C became significant, i.e., above 0.1 mmol g^{-1}, only when the CO_2 pressure reached ca. 0.2 bar. Below this pressure, no uptake could be measured reliably. Using the adsorption data for PE-MCM-41C, the corresponding values of q_{phys} for TRI-PE-MCM-41 at different temperatures were calculated taking into account the difference in surface areas, using Eq. (6) (Fig. 6, closed symbols). Data of q_{phys} thus obtained were fitted using the Toth model. The parameters of the Toth equation for the isotherms calculated for physisorption are presented in Table 2. Using data at 25 °C as reference, Fig. 6 shows that the model fits adequately the adsorption data at all temperatures. After subtraction of the calculated contribution of physical adsorption from the total CO_2 uptake measured experimentally, the profile attributed to CO_2 uptake by amines (chemisorption) closely relates to a Type I isotherm (Fig. 6, open symbols), consistent with adsorption due to chemical interactions. The Toth isotherm model

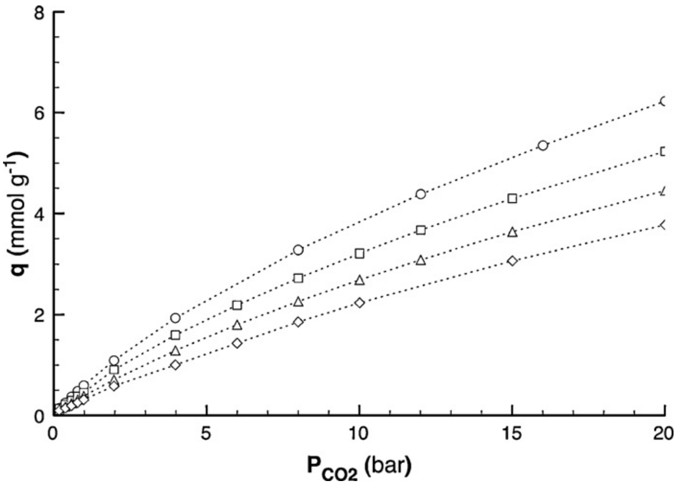

Fig. 5. CO_2 adsorption isotherm for PE-MCM-41C at 25 °C (circles), 35 °C (squares), 45 °C (triangles) and 55 °C (diamonds).

Table 1
Structural properties of mesoporous materials.

Sample	Surface area ($m^2\,g^{-1}$)	Mean pore size (nm)	Pore volume ($cm^3\,g^{-1}$)	Amine loading ($mmol_N\,g^{-1}$)	Reference
PE-MCM-41C	1134	10.88	2.26	–	This work
PE-MCM-41E	565	8.67	1.32	–	This work
TRI-PE-MCM-41	429	9.57	1.05	7.27	This work
TRI-PE-MCM-41(dry)	539	9.56	1.15	4.90	This work
SBA-15	582	9.2	0.95	–	[25]
APSBA15C	405	7.5	0.65	1.44	[25]
APSBA15U(78C, 20 h)	466	7.5	0.73	1.9	[25]
APSBA15U(50C, 20 h)	313	7.4	0.57	2.56	[25]
SBA-15	883	6.2	0.93	–	[26]
SBA15/AP1	562	5.8	0.79	1.1	[26]
SBA15/AP2	460	5.6	0.68	2	[26]

Table 2
Toth parameters of the temperature-dependent isotherm form for CO_2 adsorption on TRI-PE-MCM-41 using 25 °C as reference temperature.

CO_2 uptake	n_{s0} ($mmol\,g^{-1}$)	b_0 (bar^{-1})	t_0	χ	α	ΔH ($kJ\,mol^{-1}$)
q_{phys}	6.98	2.74×10^{-1}	9.62×10^{-1}	5.35	0	19.2
q_{chem}	3.64	1.25×10^{5}	2.24×10^{-1}	0	6.05×10^{-2}	67.3

was also applied to these data and the parameters obtained are shown in Table 2. As seen, the temperature-dependent Toth model is a good fit to the experimental values of q_{chem}, although some limitations of the model were observed in the low CO_2 pressure range at 55 °C.

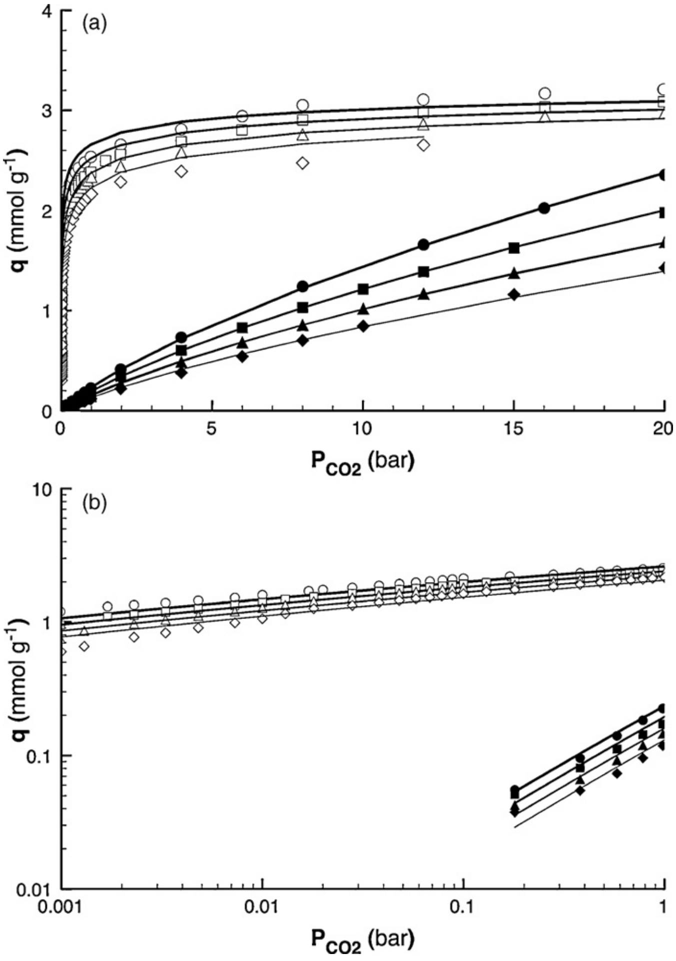

Fig. 6. q_{chem} (open symbols) and q_{phys} (closed symbols) adsorbed CO_2 in TRI-PE-MCM-41 in the (a) high and (b) low pressure range at 25 °C (circles), 35 °C (squares), 45 °C (triangles) and 55 °C (diamonds). The lines correspond to the Toth isotherm model fit.

As presented in Fig. 4, addition of q_{chem} and q_{phys} produced a model that closely matched the experimental values of q for TRI-PE-MCM-41 throughout the entire range of pressure and temperature analyzed. The calculated values of $\Delta q(\%)$ were 6.2, 5.7, 7.8 and 6.8% for the isotherms at 25, 35, 45 and 55 °C, respectively. Since the values of $\Delta q(\%)$ were less than 10% in all cases, it is inferred that the proposed methodology provides a suitable model to describe CO_2 adsorption isotherms over amine-functionalized silicas, and possibly other adsorption systems where both physisorption and chemisorption occur. It is worth noting that, although the Toth equation was used, this should not be regarded as a limitation of the proposed methodology. Since the separate contributions of physical and chemical adsorption correspond to Type I isotherms, other models could potentially be applied. However, the use of the Toth model in this work was found to be convenient to correlate the obtained parameters with physical and thermodynamic properties, such as ΔH, as will be discussed later. Another parameter of the Toth model that can provide physical meaning is n_s. The value of n_s is associated with the adsorbent uptake at saturation, in other words, the maximum amount that can possibly be adsorbed [36]. According to the generally accepted mechanisms for adsorption of dry CO_2 on amines, the limiting stoichiometry for CO_2 removal via carbamate formation corresponds to 0.5 mol of CO_2 per mol of amine. Thus, the upper limit of q_{chem} should reflect such stoichiometry, being 3.65 $mmol\,g^{-1}$ of CO_2 for an amine loading of 7.27 $mmol\,g^{-1}$ and, as seen in Table 2, this is precisely the value assigned to n_s. Furthermore, the parameter that governs the temperature dependence of n_s, i.e., χ, was found to be zero in the case of q_{chem}. This suggests that, at least within the range of temperatures analyzed, the mechanism for the chemical adsorption remains the same.

One of the assumptions used in this work was that the surface of amine-functionalized adsorbent and the surface of the pristine mesoporous silica exhibit similar behavior with regard to CO_2 physical adsorption. While such assumption vastly simplified the determination of the contribution from physical adsorption, it may seem to be too simplistic. To provide further support to this contention, a mesoporous material containing linear alkyltrimethylammonium groups, namely PE-MCM-41E (Fig. 2) was used as a reference material. PE-MCM-41E is an excellent candidate to mimic the physisorption of CO_2 on TRI-PE-MCM-41 as it contains a layer of organic groups with similar length as the tri-amine species, but without any amine functionality. Fig. 7 shows the CO_2 adsorption isotherms at 25 and 55 °C obtained experimentally for PE-MCM-41E. The isotherms exhibited a similar shape as

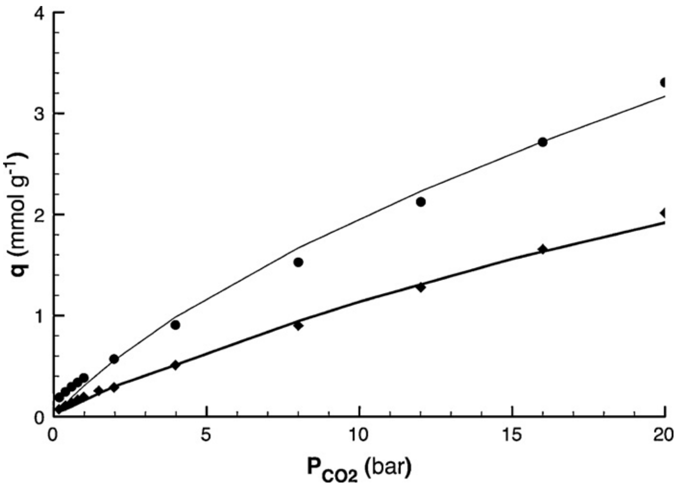

Fig. 7. Adsorption isotherms of CO_2 for PE-MCM-41E at 25 °C (circles) and 55 °C (diamonds). The lines represent the isotherms predicted using Eq. (6).

that of PE-MCM-41 (Fig. 5), although at any given CO_2 pressure, the uptake was comparatively lower. Using the values of q for PE-MCM-41C and correcting for the difference in surface areas according to Eq. (6), the adsorption isotherms for PE-MCM-41E were calculated. The predicted isotherms, included in Fig. 7, show a remarkable agreement with the experimental values, particularly at high CO_2 pressures where the contribution of physisorption is more significant. This lends strong support to the validity of the proposal to calculate q_{phys} using the more convenient silica support as a reference material for CO_2 physisorption.

To provide further support to the wide applicability of the proposed methodology, CO_2 adsorption isotherms produced experimentally for a variety of amine-functionalized mesoporous adsorbents were fitted using the new model. We first considered a sample with the same triamine species and mesoporous support but lower amine content, i.e., TRI-PE-MCM-41(dry). The adsorption isotherm of CO_2 on TRI-PE-MCM-41(dry) at 25 °C is presented in Fig. 8, along with the isotherm for TRI-PE-MCM-41 for comparison. As seen, the adsorption isotherm for TRI-PE-MCM-41(dry) also exhibits the characteristic shape described in Fig. 1. From Fig. 8, it is evident that the adsorption of CO_2 is strongly dependent on the amine content, as TRI-PE-MCM-41 has a higher adsorption capacity throughout the entire range of pressure. The methodology proposed in this work was applied to the CO_2 isotherm for TRI-PE-MCM-41(dry) and a model was produced that fits adequately the experimental data for TRI-PE-MCM-41(dry) (Fig. 8 and Table 3). Table 3 shows that n_s is the parameter whose value differs most significantly from those obtained for TRI-PE-MCM-41. This parameter affects linearly the values of q_{chem} and q_{phys} and its variation is directly related to the surface area for physical adsorption (q_{phys}) and to the amine content for chemisorption (q_{chem}). Indeed, for q_{phys}, n_s was 26% higher for TRI-PE-MCM-41(dry), compared to TRI-PE-MCM-41, reflecting the ca. 26% difference between their surface areas. For q_{chem}, the value of the n_s parameter for TRI-PE-MCM-41(dry) was ca. 62% that of n_s calculated for TRI-PE-MCM-41, which is also the ratio of the amine loading in TRI-PE-MCM-41(dry) compared to TRI-PE-MCM-41.

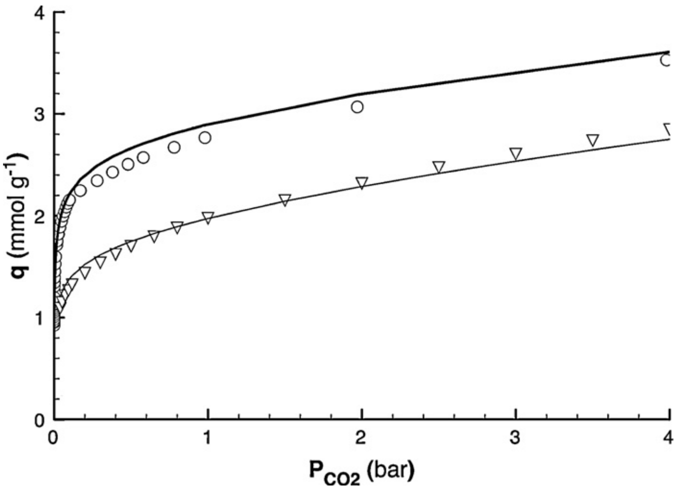

Fig. 8. CO_2 adsorption isotherms at 25 °C for TRI-PE-MCM-41(dry) (triangles) and TRI-PE-MCM-41 (circles).

The next stage was to test the model on a family of propylamine-functionalized SBA-15 mesoporous silica reported by Wang et al. [15]. This represents a challenge to the proposed methodology as these samples consisted of not only a different mesoporous support, but also a different functional group with a single primary amine group. Although details on the synthesis of these adsorbents can be found in the original work, it can be mentioned that APSBA15C was functionalized by grafting on calcined SBA-15, while APSBA15U(78C, 20 h) and APSBA15U(50C, 20 h) were functionalized by grafting on the as-synthesized SBA-15 via the so-called "one-step silylation" method, using the temperature and time indicated in parentheses. The structural properties and amine loadings of these samples are shown in Table 1. Fig. 9a shows the adsorption isotherms for these amine-grafted SBA-15 materials with the isotherm fit obtained using the proposed model. The values of $\Delta q(\%)$ were of 7.58, 5.63 and 3.25% for APSBA15C, APSBA15U(78C, 20 h) and APSBA15U(50C, 20 h), respectively, reflecting the high accuracy of the model to describe the experimental data. A particularly interesting finding is the trend observed for the Toth parameters associated with CO_2 adsorption on these samples (Table 3). Similar to TRI-PE-MCM-41, n_s was the only parameter that changed significantly from one sample to another. The values of n_s for q_{chem} were again a direct reflection of the amine content, while those for q_{phys} varied almost linearly with the surface area of the adsorbents, even when compared to our triamine-grafted adsorbent. For example, APSBA15C had a surface area and a value of n_s for q_{phys} of 94% with respect to TRI-PE-MCM-41, while the values of amine loading and n_s for q_{chem} are both ca. 20% of those for TRI-PE-MCM-41. This was a particularly important finding as it was possible to correlate the model with structural and chemical properties for a variety of amine-functionalized materials. Accordingly, it may be possible to predict the value of n_s for q_{phys}, as it was consistently equal to $0.016\,\mathrm{mmol\,m^{-2}} \times S$.

Due to these successful applications, we proceeded to test another series of adsorbents, reported by Zukal et al. [19], namely SBA-15/AP1 and SBA-15/AP2, consisting of propylamine-grafted SBA-15 with different amine loadings, as seen in Table 1. The experimental data for CO_2 adsorption reported, along with their corresponding isotherm fit are shown in Fig. 9b. Once again, excellent correlations were obtained, with values of $\Delta q(\%)$ of 2.31 and 3.38% for SBA-15/AP1 and SBA-15/AP2, respectively. In line with earlier observations, the parameter n_s changed proportionally with the surface area and amine content of each sample. Furthermore, in the case of q_{chem}, the values of the parameter b were remarkably close, not just between these samples, but also when compared to the samples described above (Table 3). In the case of q_{phys}, the parameter t remained almost constant within the various samples, with values close to 1. To provide a possible explanation to such variations, it is worth recalling the meaning of parameters b and t. Parameter b is associated with the strength of the adsorbate–adsorbent interactions [36], for which its constant value reflects the similarity of the materials under study, i.e.,

Table 3
Toth parameters of the new isotherm model for CO_2 adsorption on various amine-grafted mesoporous materials at room temperature.

Sample	q_{phys}			q_{chem}		
	n_s (mmol g^{-1})	b (bar^{-1})	t	n_s (mmol g^{-1})	b (bar^{-1})	t
TRI-PE-MCM-41(dry)	8.83	2.74×10^{-1}	9.62×10^{-1}	2.45	1.25×10^5	2.11×10^{-1}
APSBA15C	6.61	4.44×10^{-1}	9.20×10^{-1}	0.72	1.25×10^5	2.53×10^{-1}
APSBA15U(78C, 20 h)	7.60	4.44×10^{-1}	9.20×10^{-1}	0.95	1.25×10^5	2.53×10^{-1}
APSBA15U(50C, 20 h)	5.12	4.44×10^{-1}	9.20×10^{-1}	1.28	1.25×10^5	2.53×10^{-1}
SBA15/AP1	9.15	7.38×10^{-1}	9.30×10^{-1}	0.55	1.25×10^5	1.60×10^{-1}
SBA15/AP2	7.51	7.37×10^{-1}	9.30×10^{-1}	1.00	1.25×10^5	1.89×10^{-1}

in all cases q_{chem} is a result of chemical interaction of CO_2 with amine groups. The stronger bonds formed in the case of chemical adsorption are reflected in the considerably larger value of b for q_{chem} (1.25×10^5 bar^{-1}) compared to those of q_{phys} (2.7×10^{-1} to 7.38 bar^{-1}). On the other hand, t is a parameter associated with the heterogeneity of the surface, with $t = 1$ for homogeneous surfaces [36]. Since the values of t for q_{phys} were in all cases close to unity, it shows that the model obtained interpreted the available sites for physisorption as homogeneously distributed, similarly to the silica support from which it was derived. For q_{chem}, it is reasonable to assume that, because of the particular type of amines and their accessibility for each adsorbent, they presented diverse distributions of adsorption sites, with the subsequent variation in t values.

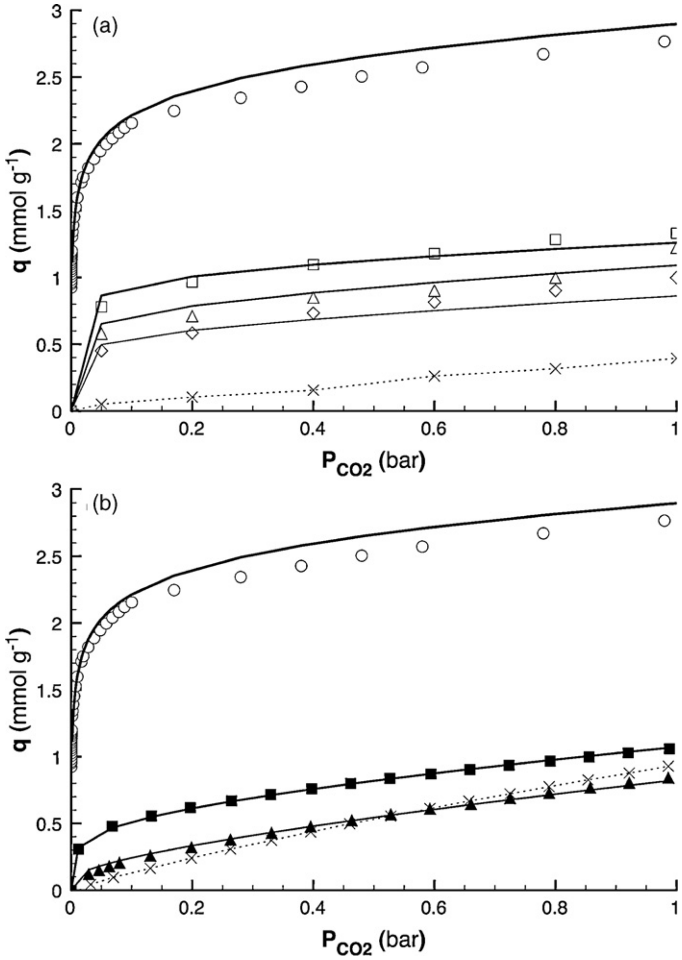

Fig. 9. CO_2 adsorption isotherms on TRI-PE-MCM-41 (circles) and: (a) APSBA15(50C, 20 h) (squares), APSBA15U(78C, 20 h) (triangles), APSBA15C (diamonds) and SBA-15 (crosses) from Wang et al. [15]; (b) SBA15/AP1 (triangles), SBA15/AP2 (squares) and SBA-15 (crosses) from Zukal et al. [19]. The solid lines correspond to the equilibrium model proposed in this work.

Since the proposed isotherm model is based on a general assumption that functionalized mesoporous silica exhibit two independent adsorption mechanisms, the applicability of the model may extend to other acid gases. Consequently, the proposed isotherm model was applied to H_2S adsorption data on TRI-PE-MCM-41 as shown in Fig. 10. Once again, the isotherm shape resembles that of Fig. 1, which can be related to the dual adsorption mechanisms. The parameters obtained for the isotherm model are shown in Table 4. The associated values of $\Delta q(\%)$ were 6.63, 1.67 and 1.65% for the isotherms at 25, 35 and 50 °C, respectively. The excellent fit of the proposed model with H_2S adsorption data on amine-modified adsorbents is a strong indication that this methodology may apply to any adsorption system that combines independent chemisorption and physisorption sites.

Fig. 11 shows the values of ΔH_{ISO} calculated using the Clausius–Clapeyron equation on the experimental adsorption data for PE-MCM-41C (Fig. 5) and TRI-PE-MCM-41 (Fig. 4). It should be noted that the evolution of ΔH_{ISO} as a function of loading presented in this work for TRI-PE-MCM-41 and the corresponding silica support are consistent with the profiles reported by other authors [13,39] using microcalorimetry for CO_2 adsorption on diamine-grafted SBA-15. High values of ΔH_{ISO} were observed in the low range of CO_2 pressure, in line with the strong interaction between CO_2 and amine groups and, as the CO_2 loading increased, ΔH_{ISO} decreased to values similar to those associated with CO_2 adsorption on silica. This trend was also observed in the case of H_2S adsorption, although lower values were obtained compared to CO_2, suggesting that weaker interactions occur with this molecule. This provides further support to the proposed model based on a combination of two adsorption mechanisms.

With respect to PE-MCM-41C, ΔH_{ISO} was found to be almost constant throughout the range of pressure studied. In addition, the value of ΔH (19.2 kJ mol^{-1}) calculated using the Toth parameter

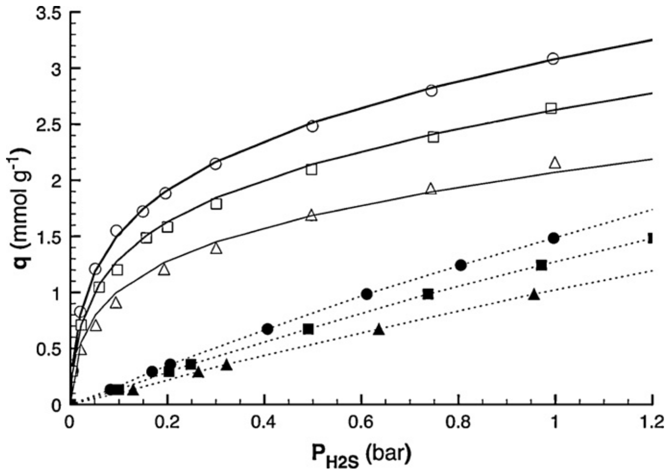

Fig. 10. Adsorption isotherms of H_2S on TRI-PE-MCM-41 (open symbols) and PE-MCM-41 (closed symbols) at 25 °C (circles), 35 °C (squares) and 50 °C (triangles). The solid lines correspond to the equilibrium model proposed in this work.

Table 4
Toth parameters of the temperature-dependent isotherm form for H_2S adsorption on TRI-PE-MCM-41 using 25 °C as reference temperature.

H_2S uptake	n_{s0} (mmol g^{-1})	b_0 (bar^{-1})	t_0	χ	α	ΔH (kJ mol^{-1})
q_{phys}	3.42	1.98×10^{-1}	9.98×10^{-1}	4.06	0	14.3
q_{chem}	7.27	4.26×10^{2}	2.22×10^{-1}	0	1.00×10^{-5}	48.3

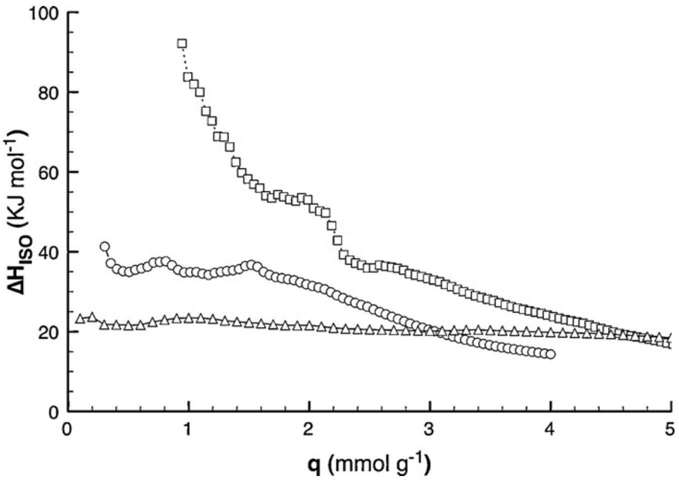

Fig. 11. Isosteric heat of adsorption for CO_2 on PE-MCM-41C (triangles), CO_2 on TRI-PE-MCM-41 (squares) and H_2S on TRI-PE-MCM-41 (circles).

b for q_{phys}, corresponds closely to that of ΔH_{ISO} on the silica support (ca. 20 kJ mol^{-1}) and is comparable to the value reported by Knowles et al. [10] and Knofel et al. [39] using calorimetry for CO_2 adsorption on mesoporous silica (i.e., 28 kJ mol^{-1} and 20 kJ mol^{-1}, respectively). It is also worth mentioning that the values of ΔH_{ISO} obtained for PE-MCM-41C are just above the enthalpy of condensation of CO_2 (ca. 17 kJ mol^{-1}) [13], indicative of weak interactions. The high values of ΔH_{ISO} at low surface coverage (Fig. 11) and the value of ΔH (67.3 kJ mol^{-1}) obtained using the Toth isotherm for the chemical interaction between CO_2 and amine groups lie within the range of values typical for chemisorption of CO_2. It is thus reasonable to assume that, in line with the model proposed, the overall heat of adsorption observed for CO_2 on the amine-grafted adsorbent is mainly a result of the strong interactions between amine groups and CO_2 at low loadings and weak interactions of CO_2 with the adsorbent surface at higher surface coverage. Similarly to CO_2 adsorption, the heat of H_2S adsorption calculated using parameters of the temperature-dependent isotherm model (Table 4) was comparable to the isosteric heat of adsorption calculated based on experimental data at low loadings (Fig. 11). Indeed, ΔH for q_{chem} was 48.3 kJ mol^{-1}, while ΔH_{ISO} at low H_2S uptake was ca. 42 kJ mol^{-1}.

4. Conclusions

Based on the observation that CO_2 adsorption on amine-functionalized mesoporous silicas occurs via two independent chemisorption and physisorption mechanisms, a semi-empirical adsorption isotherm model capable of fitting the experimental CO_2 adsorption isotherm over a wide range of pressure, from as low as 0.001 to 20 bar was developed using the Toth model in its temperature-dependent form. The heat of adsorption associated with chemisorption and physisorption, calculated using the parameters of the Toth model was consistent with experimental data, providing further physical meaning to the proposed model. The contribution of physisorption was calculated based on the assumption that at any CO_2 pressure, the amount of physisorbed CO_2 is the same as the CO_2 uptake by an equal surface area of silica support. This approach was validated using alkyltrimethylammonium-containing mesoporous silica as reference.

The model was successfully applied to different amine-functionalized materials and different adsorbates, providing strong evidence of its robustness. Moreover, the temperature-dependent form of the b parameter allowed accurate calculation of the heat of adsorption associated with chemisorption and physisorption. Another parameter, n_s, was found to be directly correlated with the surface area for physisorption and with amine content for chemisorption. Thus, within a series of related functionalized mesoporous materials the CO_2 adsorption isotherms may be predicted based on surface area and amine loading.

Acknowledgements

The financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Canadian Institute of Health Research (CIHR) is acknowledged. R.S.-G. wishes to thank the Mexican National Council of Science and Technology (CONACYT) for their support with a graduate studies scholarship. Y.B. thanks NSERC for a postdoctoral fellowship. A.S. thanks the Federal Government for the Canada Research Chair on *Nanostructured Materials for Catalysis and Separation* (2001–2015).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2010.04.024.

References

[1] B. Feng, M. Du, T.J. Dennis, K. Anthony, M.J. Perumal, Reduction of energy requirement of CO_2 desorption by adding acid into CO_2-loaded solvent, Energy Fuels 24 (2010) 213–219.
[2] Y. Li, Study on corrosion and material selection for desulphurization unit in refinery, Petroleum Refinery Eng. 38 (2008) 24–27.
[3] K. Veltman, B. Singh, E.G. Hertwitch, Human and environmental impact assessment on postcombustion CO_2 capture focusing on emissions from amine-based scrubbing solvents to air, Environ. Sci. Technol. 44 (2010) 1496–1502.
[4] R.P. Lively, R.R. Chance, B.T. Kelley, H.W. Deckman, J.H. Drese, C.W. Jones, W.J. Koros, Hollow adsorbents for CO_2 removal from flue gas, Ind. Eng. Chem. Res. 48 (2009) 7314–7324.
[5] F. Su, C. Lu, S.C. Kuo, W. Zeng, Adsorption of CO_2 on amine-functionalized Y-type zeolites, Energy Fuels 24 (2010) 1441–1448.
[6] M.G. Plaza, C. Pevida, B. Arias, M.D. Casai, C.F. Martin, J. Fermoso, F. Rubiera, J.J. Pis, Different approaches for the development of low-cost CO_2 adsorbents, J. Environ. Eng. 135 (2009) 426–432.
[7] O. Czakkel, G. Onyestyák, G. Pilatos, V. Kouvelos, N. Kanellopoulos, K. Lászlló, Kinetic and equilibrium separation of CO and CO_2 by impregnated spherical carbons, Micropor. Mesopor. Mater. 120 (2009) 76–83.
[8] H.Y. Huang, R.T. Yang, D. Chinn, C.L. Munson, Amine-grafted MCM-48 and silica xerogel as superior sorbents for acidic gas removal from natural gas, Ind. Eng. Chem. Res. 42 (2003) 2427–2433.
[9] N. Hiyoshi, K. Yogo, T. Yashima, Adsorption characteristics of carbon dioxide on organically functionalized SBA-15, Micropor. Mesopor. Mater. 84 (2005) 357–365.
[10] G.P. Knowles, J.V. Graham, S.W. Delaney, A.L. Chaffee, Aminopropyl-functionalized mesoporous silicas as CO_2 adsorbents, Fuel Process. Technol. 86 (2005) 1435–1448.
[11] F. Zheng, D.N. Tran, B.J. Busche, G.E. Fryxell, R.S. Addleman, T.S. Zemanian, C.L. Aardahl, Ethylenediamine-modified SBA-15 as regenerable CO_2 sorbent, Ind. Eng. Chem. Res. 44 (2005) 3099–3105.
[12] M.B. Yue, Y. Chun, Y. Cao, X. Dong, J.H. Zhu, CO_2 capture by as-prepared SBA-15 with an occluded organic template, Adv. Funct. Mater. 16 (2006) 1717–1722.

[13] C. Knöfel, J. Descarpentries, A. Benzaouia, V. Zelenak, S. Mornet, P.L. Llewelyn, V. Hornebecq, Functionalized micro-/mesoporous silica for the adsorption of carbon dioxide, Micropor. Mesopor. Mater. 99 (2007) 79–85.

[14] X. Liu, L. Zhou, X. Fu, Y. Sun, W. Su, Y. Zhou, Adsorption and regeneration study of the mesoporous adsorbent SBA-15 adapted to the capture/separation of CO_2 and CH_4, Chem. Eng. Sci. 62 (2007) 1101–1110.

[15] L. Wang, L. Ma, A. Wang, Q. Liu, T. Zhang, CO_2 adsorption on SBA-15 modified by aminosilane, Chin. J. Catal. 28 (2007) 805–810.

[16] J.C. Hicks, J.H. Drese, D.J. Fauth, M.L. Gray, G. Qi, C.W. Jones, Designing adsorbents for CO_2 capture from flue gas—hyperbranched aminosilicas capable of capturing CO_2 reversibly, J. Am. Chem. Soc. 130 (2008) 2902–2903.

[17] Y. Belmabkhout, A. Sayari, Effect of pore expansion and amine functionalization of mesoporous silica on CO_2 adsorption over a wide range of conditions, Adsorption 15 (2009) 318–328.

[18] X. Ma, X. Wang, C. Song, Molecular basket" sorbents for separation of CO_2 and H_2S from various gas streams, J. Am. Chem. Soc. 131 (2009) 5777–5783.

[19] A. Zukal, I. Dominguez, J. Mayerov, J. Cejka, Functionalization of delaminated zeolite ITQ-6 for the adsorption of carbon dioxide, Langmuir 25 (2009) 10314–10321.

[20] S. Couck, J.F.M. Denayer, G.V. Baron, T. Remy, J. Gascon, F. Kapteijn, An amine-functionalized MIL-53 metal-organic framework with large separation power for CO_2 and CH_4, J. Am. Chem. Soc. 131 (2009) 6326–6327.

[21] L. Hamon, P.L. Llewellyn, T. Devic, A. Ghoufi, G. Clet, V. Guillerm, G.D. Pirngruber, G. Maurin, C. Serre, G. Driver, W. van Beek, E. Jolimaitre, A. Vimont, M. Daturi, G. Ferey, Co-adsorption and separation of CO_2-CH_4 mixtures in the highly flexible MIL-53(Cr) MOF, J. Am. Chem. Soc. 131 (2009) 17490–17499.

[22] A.O. Yazaydin, R.Q. Snurr, T.H. Park, K. Koh, J. Liu, M.D. LeVan, A.I. Benin, P. Jakubczak, M. Lanuza, D.B. Galloway, J.J. Low, R.R. Willis, Screening of metal-organic frameworks for carbon dioxide capture from flue gas using a combined experimental and modeling approach, J. Am. Chem. Soc. 131 (2009) 18198–18199.

[23] J. An, S.J. Geib, N.L. Rosi, Highly selective CO_2 uptake in a cobalt adeninate metal-organic framework exhibiting pyrimidine and amino-decorated pores, J. Am. Chem. Soc. 132 (2010) 38–39.

[24] P.J.E. Harlick, A. Sayari, Applications of pore-expanded mesoporous silica. 5. Triamine grafted material with exceptional CO_2 dynamic and equilibrium adsorption performance, Ind. Eng. Chem. Res. 46 (2007) 446–458.

[25] S. Choi, J.H. Drese, C.W. Jones, Adsorbent materials for carbon dioxide capture from large anthropogenic point sources, ChemSusChem 2 (2009) 796–854.

[26] A. Sayari, Periodic mesoporous materials: synthesis, characterization and potential applications, Stud. Surf. Sci. Catal. 102 (1996) 1–46.

[27] A. Sayari, Mesoporous materials, in: P. Yang (Ed.), The Chemistry of Nanostructured Materials, World Scientific, Singapore, 2003, pp. 39–68.

[28] A. Sayari, M. Kruk, M. Jaroniec, I.L. Moudrakovski, New approaches to pore size engineering of mesoporous silicates, Adv. Mater. 10 (1998) 1376–1379.

[29] A. Sayari, Y. Yang, M. Kruk, M. Jaroniec, Expanding the pore size of MCM-41 silicas: use of amines as expanders in direct synthesis and postsynthesis procedures, J. Phys. Chem. B 103 (1999) 3651–3658.

[30] P. Selvam, S.K. Bhatia, C.G. Sonwane, Recent advances in processing and characterization of periodic mesoporous MCM-41 silicate molecular sieves, Ind. Eng. Chem. Res. 40 (2001) 3237–3261.

[31] A. Stein, B.J. Melde, R.C. Schroden, Hybrid inorganic–organic mesoporous silicates—nanoscopic reactors coming of age, Adv. Mater. 12 (2000) 1403–1419.

[32] A. Sayari, S. Hamoudi, Periodic mesoporous silica-based organic–inorganic nanocomposite materials, Chem. Mater. 13 (2001) 3151–3168.

[33] R. Serna-Guerrero, E. Da'na, A. Sayari, New insights into the interactions of CO_2 with amine-functionalized silica, Ind. Eng. Chem. Res. 47 (2008) 9406–9412.

[34] Y. Belmabkhout, R. Serna-Guerrero, A. Sayari, Adsorption of CO_2 from dry gases on MCM-41 silica at ambient temperature and high pressure. 1. Pure CO_2 adsorption, Chem. Eng. Sci. 64 (2009) 3721–3728.

[35] Y. Belmabkhout, A. Sayari, Adsorption of CO_2 from dry gases on MCM-41 silica at ambient temperature and high pressure. 2. Adsorption of CO_2/N_2, CO_2/CH_4 and CO_2/H_2 binary mixtures, Chem. Eng. Sci. 64 (2009) 3729–3785.

[36] D.D. Do, Adsorption Analysis: Equilibria and Kinetics, Imperial College Press, London, 1998.

[37] R. Serna-Guerrero, A. Sayari, Applications of pore-expanded mesoporous silica. 7. Adsorption of volatile organic compounds, Environ. Sci. Technol. 41 (2007) 4761–4766.

[38] M. Kruk, M. Jaroniec, A. Sayari, Application of large pore MCM-41 molecular sieves to improve pore size analysis using nitrogen adsorption measurements, Langmuir 13 (1997) 6267–6273.

[39] C. Knofel, C. Martin, V. Hornebecq, P. Llewellyn, Study of carbon dioxide adsorption on mesoporous aminopropylsilane-functionalized silica and titania combining microcalorimetry and in situ infrared spectroscopy, J. Phys. Chem. C 113 (2009) 21726–21734.