Adsorption 11: 237–241, 2005
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Experimental and Theoretical Analysis for the CO_2 Adsorption on Hydrotalcite

JOSÉ L. SOARES, GUSTAVO L. CASARIN, HUMBERTO J. JOSÉ, AND REGINA DE F. P. M. MOREIRA*
Departamento de Engenharia Química e Engenharia de Alimentos, Universidade Federal de Santa Catarina,
Campus Universitário, 88040-900, Florianópolis, SC, Brazil
regina@enq.ufsc.br

ALÍRIO E. RODRIGUES
Laboratory of Separation and Reaction Engineering, LSRE, Faculdade de Engenharia da Universidade
do Porto – FEUP, R Dr. Roberto Frias, 4200-465, Porto, Portugal

Abstract. The reduction of emission of carbon dioxide from flue gases can be achieved using post-combustion technologies, such as the adsorption using efficient solid sorbents. In this work, the adsorption of CO_2 on hydrotalcite was studied using dynamical and static methods. The breakthrough curves were obtained at different flow gas and total pressure 1.0 bar, using CO_2 diluted in helium at 29°C. The experimental data showed that the Freundlich model was more suitable to describe the adsorption equilibrium, and the constants of Freundlich ($k = 5.5 \times 10^{-4}$ and $n = 0.23$), are typical for favorable isotherm. The linear driving force model was suitable to describe the breakthrough curves.

Keywords: breakthrough curves, CO_2, hydrotalcite, isotherm, greenhouse gases

Introduction

The emission of carbon dioxide from burning fossil fuels has been identified as the major contributor to global warming and climate change. In the 1980's, carbon dioxide-containing flue gases contributed up to 25% of the global CO_2 emission and were responsible for 14% of the estimated global warming (Soong et al., 2001).

Separation and capture of CO_2 have been studied recently and the goal of CO_2 separation and capture is to isolate CO_2 from its many sources in a form suitable for transport and sequestration. There are three pathways for CO_2 separation: pre-combustion decarbonation, O_2/CO_2 recycle combustion and post combustion separation (Wong and Bioletti, 2004). The steam reforming of methane is a typical pre-combustion decarbonization process since the fuel is reacted with steam to produce mainly CO and H_2. The CO is reacted in a catalytic reactor to give CO_2 and more H_2. The CO_2 is separated and the hydrogen can be used as fuel or in a hydrogen fuel cell (Ding and Alpay, 2000). The autothermal reforming is a more efficient precombustion decarbonization process to produce hydrogen through the steam reforming (strongly endothermic) and partial oxidation (exothermic).

Several solids sorbents have been used to remove carbon dioxide in post combustion separation processes. Carbon molecular sieve-based material functionalized with amine groups, amine surface-bonded silica gel (Orlando et al., 1995), acrylic ester resin-based solid amine sorbent (Birbara et al., 2002) and hydrotalcites (Yong et al., 2002) are shown to be suitable adsorbents to capture CO_2 in gas phase. The ability to regenerate an adsorbent and the ease of this regeneration are also important considerations. The need for extreme conditions such as high temperatures or very low vacuum makes regeneration more complicated and costly.

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*To whom correspondence should be addressed.

Hydrotalcites are anionic clays that present layers of positively-charged metallic oxide (or metallic hydroxide) with inter-layers of anions, such as carbonates. These materials have been used as adsorbents for several applications and their use in the carbon dioxide adsorption at high temperatures was reported (Yong et al., 2002; Ding and Alpay, 2000).

In this work, we evaluated the capacity of CO_2 removal and the breakthrough curves in a fixed bed column using a hydrotalcite MG50 under different gas concentration and total flowrate.

Experimental Section

Characterization of the Adsorbent

The characterization of Puralox adsorbents (Sasol, Puralox, Germany) was performed by SEM/EDAX and N_2 adsorption at 77 K. Scanning electron microscopy/energy dispersive X-Ray (SEM/EDAX) was performed with a JEOL JSM 6301F. Elemental microprobe and elemental distribution mapping techniques were used to analyze the composition of solid. The adsorption of N_2 at 77 K was performed using an Autosorb-1 (Quantachrome, USA).

Breakthrough Curves of CO_2 Adsorption on Hydrotalcites in a Fixed Bed Column

Figure 1 shows a schematic presentation of the experimental apparatus. Prior to the tests, the hydrotalcite was pre-treated by passing pure helium at 30 mL/min and 100°C during 1 hour. The diameter and length of the column were 2.14 cm and 36.5 cm, respectively, and 1,045 pellets of adsorbent was the total capacity. The bed porosity (ε) was 0.42.

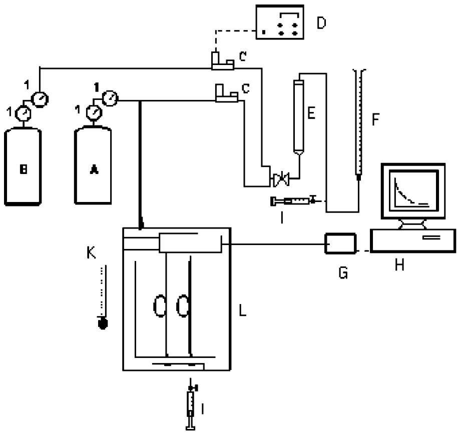


Figure 1. Schematic representation of the experimental system. (A) Helium; (B) CO_2; (C) Mass flow controller (MFC); (D) MFC control unity; (E) Adsorption column; (F) Film flowmeter; (G) Data acquisition system; (H) Computer; (I) Syringe; (K) Film flowmeter; (L) Gas Chromatograph; (1) Bourdon manometers.

After pretreatment, the temperature of the column was adjusted to 29°C and a mixture CO_2 diluted in helium was fed to a fixed bed column containing hydrotalcite MG50 The total flow gas was in the range 60 to 100 mL/min and 1.0 bar of total pressure. Different mixtures of CO_2 diluted in helium were used (3%, 10% and 20% v/v).

During the tests, aliquots of the outlet gases at the end of the column were collected at regular times and injected in a gas chromatograph (CG35 – CG Instrumentos Científicos, Brazil) equipped with a thermal conductivity detector and a Porapak-Q column.

Equilibrium of Adsorption According Static Method

The equilibrium of CO_2 adsorption at 29°C was measured in an adsorptometer (Autosorb 1C, Quantachrome, USA) in the chemisorption mode using CO_2, after pre-pretreatment of the sample for 1 hour at 100°C under high vacuum (10^{-7} torr).

Results and Discussion

Characterization of the Hydrotalcite MG50

The main characteristics of the hydrotalcite MG50 are shown in Table 1. The solid is microporous and the BET surface area is typical for these materials (Soares, 2003).

Table 1. Characterization of hydrotalcite MG50.

MgO: Al_2O_3 (%)	46.7:53.3
Pellet Length (cm)	0.45
Pellet Diameter (cm)	0.37
Pellet Volume (cm^3)	0.048
Solid Density (g/cm^3)	3.07
Pellet Density (g/cm^3)	1.13
Solid Porosity	0.63
BET Surface Area (m^2/g)	154
Micropore Volume (cm^3/g)	0.0574
Micropore Width (A)	5.53

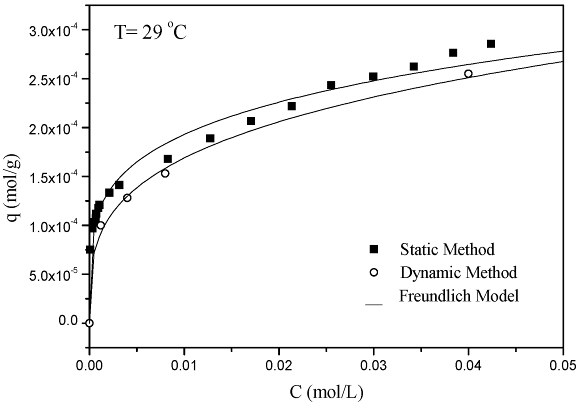


Figure 2. Equilibrium isotherm of CO_2 on hydrotalcite MG50 at 29°C.

Equilibrium of CO_2 Adsorption on Hydrotalcite MG50

The equilibrium of adsorption of CO_2 on hydrotalcite MG50 at 29°C measured by dynamical and static method is shown in Fig. 2. The experimental data were well fitted to Freundlich model while a poor correlation was found for the Langmuir model. It can be observed that both static and dynamical methods result in similar behavior, indicating that both methods are suitable to evaluate the equilibrium of adsorption.

It has been frequently discussed the possibility of CO_2 to react with hydrotalcites at low temperatures forming a carbonate, and this reaction would be the main factor to explain the high amount of CO_2 removal using these materials (Yong et al., 2002). In this case, only the thermal regeneration at high temperature could restore the adsorption capacity.

However, repeated cycles of adsorption of CO_2 on hydrotalcite MG50 and re-activation under helium at 100°C were done by Soares et al. (2002), and the results showed that the CO_2 adsorption is reversible (Soares et al., 2002) and the capacity of adsorption is restored after treatment at 100°C under helium.

The parameters of the adsorption equilibrium are shown in Table 2. The capacity of adsorption of CO_2 on hydrotalcite MG50 at 29°C is lower than the capacity using activated carbon (Soares, 2003) or zeolite 13X and 4A (Siriwardane et al., 2001). However, hydrotalcite MG50 also presents high adsorption capacity at high temperatures (Yong et al., 2002) while activated carbons presented stability problems at high temperature. The adsorption saturation capacity of hydrotalcite is insensitive or even is promoted in presence of water (Ding and Alpay, 2000) while water vapor is known to compete with CO_2 in adsorption behaviour onto zeolites (Ghosal et al., 1999). So hydrotalcite is a more suitable adsorbent to capture CO_2 in a large range of temperature.

Table 2. Equilibrium parameters for the adsorption of CO_2 on hydrotalcite MG50 at 29°C.

		Static method	Dynamical method
Freundlich model	10^4 K	5.5 ± 0.2	6.3 ± 0.5
	n	0.228 ± 0.010	0.286 ± 0.019

Breakthrough Curves

The entalphy of CO_2 adsorption on hydrotalcite is too low and no important heat effects are expected using CO_2 concentration lower than 20%, as previously reported by Ding and Alpay (2000).

The breakthrough curves to the adsorption of CO_2 on hydrotalcite MG50 at 29°C is shown in Fig. 3. It can be observed that the breakthrough is abrupt, indicating that the porous media is not dispersive and the breakthrough curves are symmetrical. Different CO_2 concentration in inlet of the column resulted in the curves shown in Fig. 3(a). The effect of the gas flowrate is shown in Fig. 3(b).

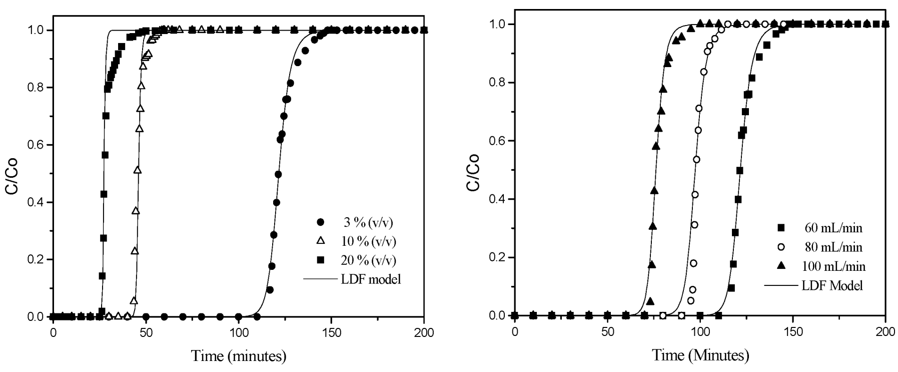
For the CO_2 feed concentration of 3% (v/v) and different gas flowrate, it was observed that the stoichiometric times, t_{st}, (calculated by Eq. (1) are different, but the mass balance (calculated by Eq. (2) showed identical capacity of adsorption, confirming the quality of the experimental data.

$$t_{\mathrm{St}} = \int_0^\infty \left(1 - \frac{C}{C_o}\right) dt \tag{1}$$

$$q = \frac{Q \cdot C_o \cdot t_{\mathrm{St}}}{V \cdot (1-\varepsilon)} - \frac{\varepsilon \cdot C_o}{(1-\varepsilon)} \tag{2}$$

The rate of mass transfer of CO_2 to the solid was described according to the linear driving force model. The mass balance equation and boundary conditions are presented in Eqs. (3) to (6). The global mass balance is given by Eq. (3) (Ruthven, 1984).

$$\frac{\partial C}{\partial \theta} + \frac{\rho_L}{\varepsilon}\frac{\partial \bar{q}}{\partial \theta} = \frac{1}{\mathrm{Pe}}\frac{\partial^2 C}{\partial x^2} - \frac{\partial C}{\partial x} \tag{3}$$



(a) (b)

Figure 3. Breakthrough curves for the adsorption of CO_2 on hydrotalcite MG50: (a) different initial CO_2 concentration (total flowrate 60 mL/min and total pressure 1.0 atm); (b) different total flowrate (CO_2 concentration 3% v/v and total pressure 1.0 atm).

The rate of mass transfer inside the particle is described by Eq. (4) and the mass transfer in the film around the particle is given by Eq. (5) (Ruthven, 1984).

$$\frac{\partial \bar{q}}{\partial \theta} = K_S \tau (q^* - \bar{q}) \tag{4}$$

$$\frac{\partial \bar{q}}{\partial \theta} = K_F a \tau (C - C_S) \tag{5}$$

The initial and boundary conditions are presented in Eq. (6) (Ruthven, 1984).

$$\begin{aligned} &\theta = 0 : \bar{q} = 0; \quad C = 0; \quad C_S = 0 \\ &x = 0 : -\frac{1}{\text{Pe}} \cdot \frac{\partial C}{\partial x} + C = C_{\text{Feed}}; \ \bar{q} = 0, \quad C_S = 0 \\ &x = 1 : \frac{\partial C}{\partial x} = 0; \quad \frac{\partial \bar{q}}{\partial x} = 0; \quad \frac{\partial C_S}{\partial x} = 0 \end{aligned} \tag{6}$$

The breakthrough curves were simulated using the parameters shown in Table 3. The Eqs. (3) to (6) were solved using a software in *Fortran* language using the orthogonal collocation method.

The simulated curves are presented in Fig. 3(a) and (b). Excellent agreement was obtained to all experimental conditions indicating that the LDF model is suitable to describe the adsorption of CO_2 on hydrotalcite MG50 in a fixed bed. The values of molecular diffusity coefficient (D_m), Knudsen diffusivity coefficient (D_K) and K_S are 0.592 cm^2/s, 1.042 $\times 10^{-3}$ cm^2/s and 1.985 min^{-1}, respectively, for all breakthrough curves. The capacity of adsorption of CO_2 on hydrotalcite at 29°C is lower than that of activated carbon or zeolites but it is a suitable adsorbent to capture CO_2 to control greenhouse effect due to water coadsorption insensitivity.

Table 3. Parameters used for the simulation of breakthrough curves.

% CO_2 (v/v)	Flowrate (mL/min)	Re	Pe[a]	Sc	Sh	K_F (cm/s)
3	60	0.16	34.4	1.50	2.43	2.75
	80	0.22	34.6	1.50	2.51	2.86
	100	0.27	34.7	1.50	2.57	2.93
10	60	0.26	34.7	0.94	2.48	2.82
20	60	0.40	35.0	0.60	2.53	2.88

[a] Peclet number was evaluated according Leitão and Rodrigues (1995).

Nomenclature

a	External superface area for unit of volume of the pellet, cm^{-1}
C	Molar concentration in the bulk phase, mol/L
C_o	Initial molar concentration, mol/L
C_S	Molar concentration on surface of the pellet, mol/L
k	Equilibrium constant of Freundlich isotherm
K_F	Film mass transfer coefficient, cm/s
K_S	Internal mass transfer coefficient, s^{-1}
n	Parameter of Freundlich isotherm
Pe	Peclet number
q	Adsorbed concentration, $mmol/g_{\text{Pellet}}$
$\bar{q}$	Adsorbed phase average concentration, $mmol/g_{\text{Pellet}}$
q^*	Adsorbed concentration at equilibrium, $mmol/g_{\text{Pellet}}$

Q	Flowrate, mL/min
Re	Reynolds number, $[\rho \cdot v \cdot d_{eq}/\mu]$
Sc	Schmidt number, $[\mu/\rho \cdot D_m]$
Sh	Sherwood number, $[K_F \cdot d_{eq}/D_m]$
t	Time, min
t_{St}	Stoichiometric time, min
V	Bed volume, cm^3
x	Dimensionless axial coordinate in the bed
ε	Total bed porosity,
μ	Viscosity, kg/ms
θ	Dimensionless time, $[t/\tau]$
ρ_L	Bed density, kg/L

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