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Wastes: Solutions, Treatments and Opportunities

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Preface

Dear colleagues,

It is with great pleasure that we bring to you the book "Selected papers from the 3rd edition of the International Conference Wastes: Solutions, Treatments and Opportunities".

The papers published in this book were submitted, revised and approved by the Scientific Committee in a full peer review process to be presented at Wastes 2015 that took place in the Polytechnic Institute of Viana do Castelo, between 14 and 16 of September.

The Wastes conferences, happening every two years, are a platform for the scientists and industries from the waste management and recycling sectors from around the world, to share experiences and knowledge with all who attend. Discussions regarding the balance between economic, environmental and social outcomes are carefully addressed. The development of innovative techniques, tools and strategies on how wastes can be transformed into good ideas, improving both the overall environmental performance and the understanding of the industry impact on the environment, as well as the options analysis for its improvement are key objectives of this conference.

With this publication we expect to take the scope of this event beyond the limits of its physical occurrence by providing both attendants and general public with an instrument that is the materialization of the main contributions to Wastes 2015.

The editors wish to thank all the reviewers that, taking part of the Scientific Committee of the Conference, gave a fundamental input to the process of reviewing the papers included in this book, namely:

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Fixed bed adsorption dynamics of CO_2/CH_4 mixtures in zeolite 13X for biogas upgrading

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ABSTRACT: The separation performance of CO_2/CH_4 mixtures in binderless beads of zeolite 13X has been studied in a fixed bed adsorption system for biogas upgrading strategies to biomethane. Zeolite 13X proved to be very efficient for the separation leading to breakthrough curves that show a plateau of pure CH_4 of approximately 4 minutes depending of the operating conditions chosen. The separation performance for CO_2/CH_4 measured by the selectivities range from 37 at a low pressure of 0.1 MPa to approximately 5.0 at the high temperature of 423 K. A mathematical model for fixed bed adsorption studies was used and validated through the experimental data predicting with good accuracy the behavior of the transient breakthrough experiments being a valuable tool for the analysis and design of cyclic adsorption processes (PSA) for biogas upgrading strategies to biomethane and CO_2 capture using 13X zeolite.

1 INTRODUCTION

Biogas is a raw gaseous stream produced by the anaerobic decomposition of organic matter in units called digesters. It is mainly composed by CH_4 (50 to 70%) and CO_2 (30 to 40%) and to obtain a high energy content CO_2 needs to be separated from CH_4. Major sources of biogas production are landfills, waste-water treatment plants, manure fermentation, fermentation of energy crops and coal-bed methane. To increase the heating value of the biogas it's necessary to remove CO_2 and the upgraded biogas can be used as a vehicle fuel in cars and buses or injected in the natural gas grid of a city or power plant.

Two recent reviews discuss this matter with great detail concerning the use of adsorbents (porous solids) based technologies to handle CO_2 capture and CO_2/CH_4 separations (Férey et al., 2011; D'Alessandro et al., 2010). For this purpose many solid physical adsorbents have been considered including molecular sieve zeolites and a new class of adsorbents named Metal-Organic Frameworks (MOFs). Zeolite 13X is still one promising adsorbent to capture CO_2 because of the strong adsorbate-adsorbent interactions (D'Alessandro et al. 2010). One of the technologies for biogas upgrading to biomethane using adsorbents is called Pressure Swing Adsorption (PSA). With this technique, carbon dioxide is separated from the biogas by adsorption in a proper adsorbent under elevated pressure. The adsorbent material, is regenerated by a sequential decrease in pressure before the column is reloaded again, hence the name of the technique. A review about the use of PSA technology for biogas upgrading is described in detail by Grande, 2011.

The modelling of fixed bed adsorption dynamics is of fundamental importance for the design of industrial adsorbers due to the complexity of these systems, that involve several mechanisms for mass and heat transfer coupled with thermodynamic models that describe the equilibrium adsorption between gas and solid phases.

In this work, we present fixed bed adsorption transient experimental data with single and multicomponent mixtures of CO_2 and CH_4 on binderless beads of zeolite 13X at 313, 373 and 423 K and pressures ranging from 0.1 to 0.5 MPa. A transient mathematical fixed bed adsorption model taking into account mass and energy conservation laws is used to capture the fixed bed adsorption experimental data, which could be used in the implementation (simulation) of cyclic adsorption processes (PSA, TSA) for the purification of biogas or CO_2 sequestration.

2 THEORETICAL

2.1 *Mathematical model to study fixed bed adsorption dynamics*

The modelling of fixed bed adsorption dynamics is very important to the design of cyclic adsorption processes to operate at industrial scale. The model should take into account the conservation laws of mass and energy in the fixed bed coupled with the thermodynamic (adsorption equilibrium isotherms) and kinetics (mass transfer rate of adsorbable species to solid adsorbent) of sorption characteristic of a certain system.

Let us consider that at time zero a mixture of known composition is introduced at the inlet of a fixed bed containing a suitable adsorbent for the separation of the mixture. If the following assumptions are made:

1. Ideal gas;
2. There is no pressure drop in the column;
3. The flow pattern is described by the axial dispersed plug flow model;
4. The mass transfer between bulk gas phase and adsorbent particle is accounted by a Linear-Driving-Force model (LDF);
5. The system is non-isothermal and non-adiabatic;
6. A resistance to heat transfer between solid adsorbent and bulk gas phase could exist in the external fluid film around the solid;
7. There is no temperature gradients inside the porous adsorbents (the temperature is homogeneous in the solid).

Silva (1998) according to these assumptions developed a mathematical model to simulate the fixed bed adsorption of gaseous mixtures and PSA cycles in adsorbent materials.

2.2 *Thermodynamic adsorption model*

Coupled with the mathematical fixed bed adsorption model we must have a suitable thermodynamic adsorption equilibrium description for the system since the transient response of the bed at the outlet will depend dramatically of the efficacy of such model. There are in literature several idealized adsorption isotherm models to describe the equilibrium distribution of guest molecules and host porous adsorbents. In a previous work it has been shown that an appropriate model to describe the binary sorption behavior of CO_2 and CH_4 on binderless zeolite 13X is the Fowler model (Silva et al., 2012) which is described by the following equations,

$$\frac{1}{p_1}\frac{\theta_1}{1-(\theta_1+\theta_2)} = b_1\exp\left(-\frac{w_{11}\theta_1}{RT}-\frac{w_{12}\theta_2}{RT}\right) \tag{1}$$

$$\frac{1}{p_2}\frac{\theta_2}{1-(\theta_1+\theta_2)} = b_2\exp\left(-\frac{w_{22}\theta_2}{RT}-\frac{w_{12}\theta_1}{RT}\right) \tag{2}$$

where $\theta = q/q_m$ is the degree of filling of sites, b is an equilibrium constant, p the pressure, q the amount adsorbed and q_m is the amount adsorbed at the saturation of the adsorbent, w is the extra energy when sorbate molecules occupy adjacent sites, R the ideal gas constant and T the temperature. The subscripts 1 and 2 refer to the adsorbable species (1) (CO_2) and 2(CH_4) along the manuscript. Table 1 show the adsorption equilibrium model parameters.

Table 1. Isotherm model parameters for single and binary sorption of CO_2 and CH_4 in binderless beads of 13X zeolite (data from Silva et al. 2012).

		$CO_2(1)$		$CH_4(2)$
q_m	(mol/kg$_{ads}$)	7.4		7.4
ΔH	(kJ/mol)	−43.1		−8.9
w_{11}	(kJ/mol)	12.3		–
w_{22}		–		–
		313 K		
b	(atm^{-1})	21.3		0.0643
$-w_{12}/RT$	(–)		1.39	
		373 K		
b	(atm^{-1})	1.49		0.0374
$-w_{12}/RT$	(–)		1.25	
		423 K		
b	(atm^{-1})	0.286		0.0256
$-w_{12}/RT$	(–)		1.10	

3 EXPERIMENTAL

3.1 *Adsorbent and adsorbates*

The powder of 13X from which the binderless beads were formed is from Chemiewerk Bas Kostritz GmbH (Germany) with a Si/Al ratio of 1.18. Metakaolin is used to manufacture the beads. The synthesis and characterization procedure is described in detail elsewhere (Schumann et al., 2012). Briefly, the beads formed consist in spherical particles with a diameter ranging from 1.2 to 2.0 mm. The size of the zeolite crystals are around 2 μm.

The sorbate and inert gases were furnished by Air Liquid with the following purities: methane N35 (99.95%), carbon dioxide N48 (99.998%), and helium ALPHAGAZ 2 (99.9998%).

3.2 *Single and multicomponent fixed bed experiments*

To study of the adsorption of CO_2 and CH_4 in the fixed bed was performed in a stainless steel column of 4.6 mm i.d. with 80 mm length containing the zeolite 13X beads which were placed inside a chromatographic oven with automatic temperature control. A typical experiment consists in measuring continuously the transient concentration histories at the outlet of the column using a thermal conductivity detector (TCD) and a mass spectrometer (MS) after feeding the column with a single component or mixtures of CO_2 and CH_4 of known composition. When the saturation is reached, the column is regenerated being prepared for another run. Details of the apparatus and experimental procedure can be found in detail elsewhere (Bastin et al., 2008).

4 RESULTS AND DISCUSSION

Breakthrough curves or the transient response at the outlet of the bed to an input of a single component or mixture feed at inlet is the more realistic way to evaluate the performance of an adsorbent for a specific separation or encapsulation of compounds. In the present study, several breakthrough curves were performed by feeding a fixed bed column containing beads of zeolite 13X with CO_2 or CH_4 or a mixture of both to evaluate the separation performance of the fixed bed adsorption system.

4.1 *Single component fixed bed adsorption experiments of CO_2 and CH_4*

Figure 1 shows two typical experimental breakthrough experiments obtained for the sorption of CO_2 (Figure 1a) and CH_4 (Figure 1b) at 313 K and total pressure in the column of 0.1 MPa. The

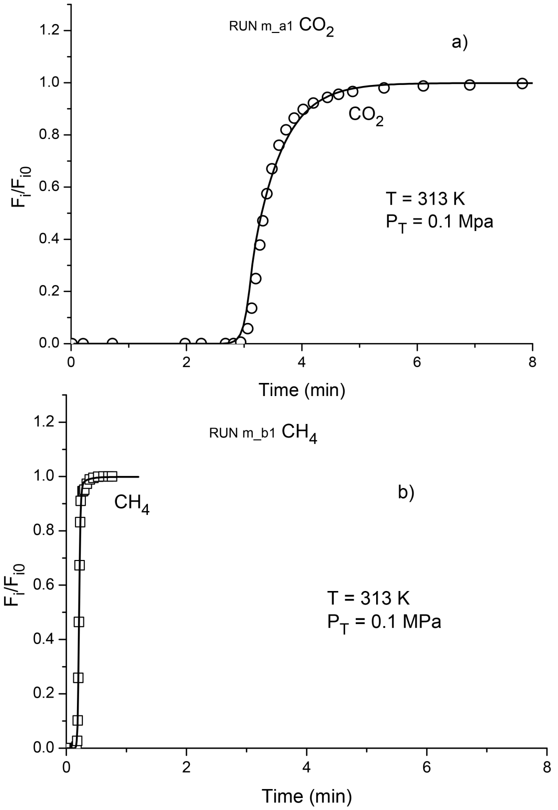

Figure 1. Single component experimental breakthrough curves (points) on binderless beads of 13X zeolite at 313 K and total pressure 0.1 MPa and comparison with the mathematical model (lines). (a) CO_2 feed at 21.7 Nml/min diluted in helium at 21.8 Nml/min. (b) CH_4 feed at 21.8 Nml/min diluted helium at 19.3 Nml/min. The simulation of the experimental runs with the mathematical model and respective parameters and correlations were adapted from the work of Silva (1998).

breakthrough time of CO_2 starts at 3 min spreading to the final input concentration at near 6 min. On the contrary, CH_4 (Figure 1b) breaks the column in much less than 1 min (practically with no adsorption) with a sharpening front. These results show that zeolite 13X has a strong affinity for CO_2 at 313 K being the sorption of CH_4 practically negligible. This means that we can predict that in mixture sorption zeolite 13X is able to separate with great efficiency CO_2 from binary mixtures of CO_2/CH_4 with a very high selectivity. At the same time, we can also conclude that the capacity of zeolite 13X to sequestrate CO_2 is very high being a good alternative to be used in systems where it is necessary to capture it. For the experiment reported in Figure 1a the amount adsorbed of CO_2 is around 3.8 mol/kg which can be considered a very high value at a total pressure in the column around 0.1 MPa. The lines in the figures represent model predictions and we can also conclude that the mathematical model capture with good accuracy the concentration profile of the transient breakthrough curves.

4.2 *Binary CO_2/CH_4 fixed bed adsorption experiments*

In strategies for biogas upgrading we wish to separate CO_2 from CH_4 by feeding the fixed bed column with mixtures of known composition and separate CH_4 from CO_2. When in contact with the adsorbent, the mixture is selectively adsorbed in the fixed bed due to differences in the adsorption strengths between the compounds, giving rise to the formation of different mass travelling waves

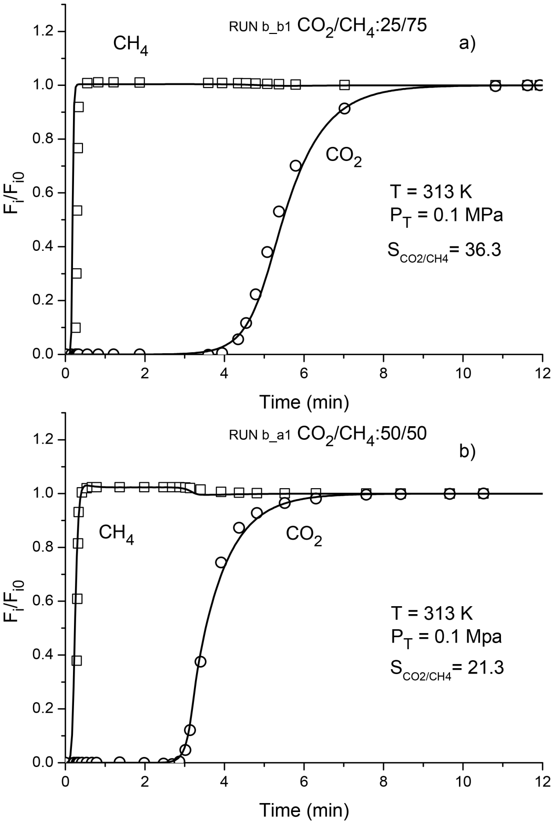

Figure 2. Binary CO_2/CH_4 experimental breakthrough curves (points) on binderless beads of 13X zeolite at 313 K and 0.1 MPa and comparison with the mathematical model (lines). (a) Binary mixture with $25(CO_2)/75(CH_4)$ feed at 9.2 Nml/min CO_2, 26.9 Nml/min CH_4 diluted in helium at 19.2 Nml/min. (b) Binary mixture with $50(CO_2)/50(CH_4)$ feed at 16.5 Nml/min CO_2, 16.5 Nml/min CH_4 diluted in helium at 16.5 Nml/min. The simulation of the experimental runs with the mathematical model and respective parameters and correlations were adapted from the work of Silva (1998).

along the bed, resulting in a transient breakthrough curve at the outlet with a different composition of the one at bed inlet until it is completely saturated. To demonstrate this, we present two typical binary breakthrough curves obtained after feeding the column with mixtures of CO_2/CH_4. Figure 2a shows an experimental breakthrough curve after feeding the column with a $50(CO_2)/50(CH_4)$ and Figure 2b with a $25(CO_2)/75(CH_4)$ mixture diluted with helium (inert) at the temperature of 313 K and total pressure in the column of 0.1 MPa. Figure 2a clearly shows a complete separation between CO_2 and CH_4 with a long plateau of pure CH_4 of almost 4 min for the 25/75 mixture ratio. The selectivity measured by the ratio of the amounts adsorbed of the two components is $S_{CO2/CH4} = 36.3$. Also interesting is the fact that Figure 2a,b shows that CH_4 breaks the column practically at the beginning of the experiment. Remarkable also is that the mass transfer zone for CH_4 is very sharp which very interesting for separation purposes. In Figure 2b for the 50/50 mixture ratio the selectivity decrease ($S_{CO2/CH4} = 21.3$) but it can be considered also very high. At the same time, the lines in the figures show that the mathematical model developed is also capable to capture with good accuracy the concentration profiles of both compounds as well as the plateaus of pure CH_4 observed experimentally in mixture sorption, being a valuable tool for the design of cyclic industrial processes (PSA).

Table 2. Selectivities as a function of temperature and total mixture pressure for several binary 50/50 and 25/75 binary, obtained from several breakthrough experiments.

Total Pressure	$50(CO_2)/50(CH_4)$			$25(CO_2)/75(CH_4)$		
(MPa)	313 K	373 K	423 K	313 K	373 K	423 K
0.5	10.4	6.4	5.4	14.4	8.7	6.8
0.3	11.3	7.9	5.5	19.7	10.8	7.1
0.1	21.3	16.6	7.4	36.3	19.8	10.3

4.3 *Selectivities for several CO_2/CH_4 fixed bed experiments*

Table 2 resumes the selectivities obtained for several 50/50 and 25/75 CO_2/CH_4 mixture breakthrough experiments as a function of total pressure. Table 2 shows that the selectivities are high at the low temperature of 313 K and total pressure 0.1 MPa being 36.3 (Experiment – Figure 2a) and 21.3 (Experiment – Figure 2b) for the 25/75 and 50/50 mixtures, respectively. As the pressure increases the selectivities decrease but the values are still considerable high at 313 K and total pressure of 0.5 MPa ranging from 14.4 to 10.4 for the 25/75 and 50/50 mixtures ratios, respectively. These results show that binderless beads of 13X zeolite can be considered an excellent separator of mixtures CO_2/CH_4 when appropriate operating conditions are chosen.

5 CONCLUSIONS

Through this work we show an experimental study of the sorption of single and binary mixtures of CO_2 and CH_4 in binderless beads of 13 X zeolite. The single component transient fixed bed adsorption experiments performed with CO_2 show that zeolite 13X in very efficient to encapsulate it. However, with CH_4 we see a complete different picture where the compound practically breaks the columns at beginning of the experiment practically with no adsorption. The efficiency of the separation of mixtures CO_2/CH_4 in the binderless beads of 13X zeolite starting from a fresh column is illustrated through two binary breakthrough curves where it is clearly seen the ability of zeolite 13X to separate CO_2 from CH_4 . These results show that zeolite 13X is a good choice for strategies of upgrading biogas to biomethane. For other conditions, Table 2 resumes the selectivities obtained from several mixture breakthrough experiments with values ranging from 37 at the low pressure of 0.1 MPa and temperature of 313 K to approximately 5 at the high temperature of 423 K.

A mathematical fixed bed adsorption dynamic model coupled to the thermodynamic model of adsorption of Fowler was used and validated through the experimental data proving to be a valuable tool for the design of cyclic adsorption processes for biogas upgrading to biomethane (by PSA) and CO_2 capture.

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