Available online at www.sciencedirect.com
SCIENCE DIRECT
Separation and Purification Technology 49 (2006) 91–100
Separation Purification Technology
www.elsevier.com/locate/seppur

Fixed-bed adsorption of carbon dioxide–helium, nitrogen–helium and carbon dioxide–nitrogen mixtures onto silicalite pellets

José A. Delgado *, María A. Uguina, José L. Sotelo, Beatriz Ruíz

Department of Chemical Engineering, Universidad Complutense de Madrid, 28040 Madrid, Spain

Received 10 June 2005; received in revised form 27 July 2005; accepted 31 August 2005

Abstract

In this work, the fixed-bed adsorption of carbon dioxide and nitrogen on silicalite pellets has been studied. Adsorption equilibrium and kinetic measurements of carbon dioxide and nitrogen on this adsorbent at several temperatures have been performed, and the single adsorption equilibrium isotherms have been obtained for both adsorbates. A model based on the LDF approximation for the mass transfer, taking into account the energy and momentum balances, has been used to describe the adsorption kinetics of carbon dioxide and nitrogen as single components. The model reproduced satisfactorily the breakthrough curves obtained with carbon dioxide–nitrogen mixtures.

Keywords: Carbon dioxide; Nitrogen; Silicalite; Adsorption; Fixed-bed; Modeling

1. Introduction

The discharge of carbon dioxide into the atmosphere due to the consumption of large amounts of fossil fuels has become one of the most serious global environment problems, which is now being paid attention to by public authorities worldwide. These emissions mainly contain carbon dioxide and nitrogen. Separation of carbon dioxide by means of a PSA process from these effluents is feasible [1]. Several patents also demonstrate the interest of this separation [2,3].

In its purified form, carbon dioxide has many uses in the chemical industry. It can be used in solid form (dry ice), liquid form (in refrigeration equipment), or gaseous form (for example, in carbonated beverages and in fire extinguishing equipment), or even in the supercritical state (supercritical extraction). The concentration and recovery of carbon dioxide from flue gases using activated carbon, and the separation of carbon dioxide from carbon dioxide–nitrogen mixtures diluted in helium using zeolite 13X, both performed by means of a PSA process, have been addressed in the literature [4,5]. The main requirement for a PSA cycle to be applicable to the separation of carbon dioxide–nitrogen mixtures is to find an adsorbent selective to one of these compounds. It is also necessary that the affinity of the adsorbent to the selected component is not too high, because otherwise the regeneration step can negatively affect the economy of the process. Also, the uptake rates must be high enough to achieve a reasonable productivity. Among all the commercial adsorbents available to perform this separation, zeolites are possible candidates, as they have high selectivities for carbon dioxide, because of the polar character of this adsorbate. However, carbon dioxide adsorption on these adsorbents is typically too strong, which makes desorption difficult. A further consideration on the selection of the adsorbent concerns possible effects of the impurities in flue gas, such as water, sulphur dioxide and nitrogen oxides. It is desirable that these impurities do not affect carbon dioxide adsorption. Hydrophobic zeolites, such as silicalite and USY, having low aluminum content, show a good compromise between high carbon dioxide selectivity and easy regeneration, according to literature data [6,7]. As only non-specific interactions (dispersion plus polarization) are involved, the desorption rate of carbon dioxide from these zeolites is significantly higher than from the hydrophilic ones, where the quadrupole moment of carbon dioxide dominates the interaction. Moreover, hydrophobic zeolites, unlike their hydrophilic counterparts, can be used in adsorption systems for carbon dioxide recovery in the presence of water vapor, as their adsorption capacity is not drastically reduced in this case [8].

The design of a PSA system also requires the development of a model that can describe the dynamics of adsorption on a fixed-bed of the selected adsorbent, taking into account all

* Corresponding author. Tel.: +34 91 3944119; fax: +34 91 3944114.
E-mail address: jadeldob@quim.ucm.es (J.A. Delgado).

1383-5866/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.seppur.2005.08.011

the relevant transport phenomena. In this work, the fixed-bed adsorption of carbon dioxide and nitrogen on silicalite pellets has been studied. Adsorption equilibrium and kinetic measurements of carbon dioxide and nitrogen on this adsorbent at several temperatures have been performed, in order to obtain the single adsorption equilibrium isotherms. A model based on the LDF approximation for the mass transfer, taking into account the energy and momentum balances, has been used to describe the adsorption kinetics of carbon dioxide and nitrogen as single components. The model has been employed to analyze the breakthrough behavior of mixtures of carbon dioxide and nitrogen on silicalite.

2. Experimental

All the gases used in this work had purity higher than 99.5%, supplied by Praxair. The adsorbent used was a commercial agglomerated silicalite (30% binder) in the form of cylindrical pellets, supplied by CECA. Adsorbent properties are shown in Table 1.

Adsorption experiments were performed by feeding gas mixtures to a column packed with the adsorbent. The remaining void column volume was filled with glass beads. Fixed-bed properties are given in Table 1. A scheme of the experimental setup is shown in Fig. 1. The flow of each gas was controlled with mass flow controllers (Bronkhorst). The adsorbent was regenerated after each adsorption experiment by evacuation for 30 min, and feeding helium afterwards for 30 min. The column was located inside a convective furnace with controlled temperature, except for the experiments at 298 K, for which the room temperature was controlled. The flow rate at the bed exit was measured with a bubble meter. Adsorbent temperature was monitored with a thermocouple located at 9 cm from the bed entrance. A Varian 3800 gas chromatograph fitted with a 3 m × (1/8) in. stainless steel column packed with Porapak Q (Supelco) and equipped with TCD detector was employed for monitoring the carbon dioxide and nitrogen concentration at the bed exit, using helium as the reference gas. The chromatograph was equipped with a sampling valve with a loop of 0.25 ml, which was continuously filled with the gas entering the chromatograph, and connected to the chromatograph column at different times. All the connections are made of Teflon and stainless steel tubing ((1/8) in.).

Table 1
Properties of the adsorbent and the fixed-bed

Adsorbent	
Pellet radius	$R_p = 0.0007$ m (cylindrical)
Particle density	$\rho_p = 1070\ \mathrm{kg\,m^{-3}}$
Crystal size	$r_c = 3 \times 10^{-6}$ m
Particle porosity	$\varepsilon_p = 0.77$ (extra- and intracrystalline)
Solid heat capacity	$c_{p,s} = 1000\ \mathrm{J\,kg^{-1}\,K^{-1}}$
Fixed-bed	
Bed length	$L = 0.163$ m
Bed weight	$W = 0.0169$ kg
Bed internal diameter	$d_i = 0.016$ m
Bed voidage fraction	$\varepsilon = 0.52$
Column wall thickness	$l = 0.002$ m
Wall heat capacity	$c_{p,w} = 500\ \mathrm{J\,kg^{-1}\,K^{-1}}$
Wall density	$\rho_w = 8000\ \mathrm{kg\,m^{-3}}$

3. Model description

The model used to describe the fixed-bed dynamics is derived from the mass, energy and momentum balances, including the following assumptions:

(i) The flow pattern is described with the axially dispersed plug flow model.
(ii) Local thermal equilibrium is assumed between the gas and the adsorbent particles.

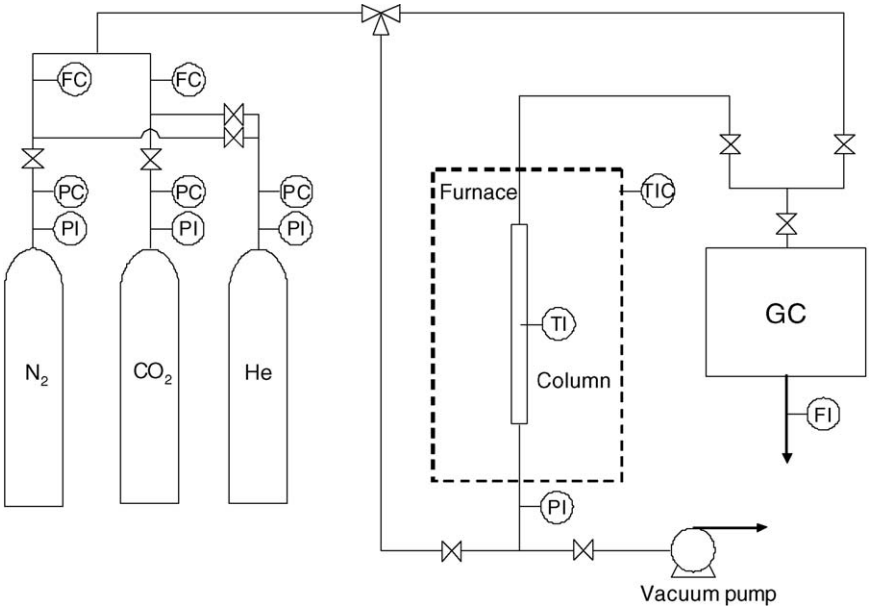

Fig. 1. Scheme of the setup for the fixed-bed adsorption experiments.