Fixed bed adsorption for the removal of carbon dioxide from nitrogen: Breakthrough behaviour and modelling for heat and mass transfer

V.P. Mulgundmath, R.A. Jones, F.H. Tezel *, J. Thibault

Department of Chemical & Biological Engineering, University of Ottawa, 161 Louis Pasteur, Ottawa, Canada K1N 6N5

1. Introduction

Carbon dioxide is an omnipresent species that has generated enormous attention since the turn of the century because of its contribution to the greenhouse gas effect. Combustion of fossil fuels is a major source of these harmful emissions which is the result of ever increasing world wide population and an increased per capita demand for energy. According to the International Energy Agency Working Party on Fossil Fuels [1], more than 85% of the world's energy needs are met by fossil fuels which account for the annual emission of 25 billion tons of CO2 into the atmosphere. Fossil fuel-fired power generation facilities account for one-third of the global CO2 emission to the atmosphere [2]. This has resulted in a global research effort to mitigate the emissions of CO2 and examine ways to capture CO2 directly from power plant flue gases [3].

For the purpose of reducing CO2 emissions to the atmosphere, IEA WPFF [1] outlines the utilisation of Zero Emission Technologies (ZET) which virtually eliminate emissions from the conversion of fossil fuels and their consequences on health and environment. ZET promote the increase of the overall plant efficiency, the use of lower-carbon or carbon free energy sources, oxy-fuel combustion, CO2 fixation using algae and the development of new power cycles. However, these are innovative technologies that cannot be easily used to retrofit existing power plants. Carbon sequestration involving the carbon dioxide capture and storage (CCS) has become a major focus of reducing point-source emissions. For CO2 to be sequestered, it must be relatively pure (>95%) to find useful applications in the food refrigeration industry, fire extinguishers, enhanced oil recovery, beverage carbonation, metals fabrication, urea production and gas reservoirs competition with adsorption processes for CO2 removal [5,6]. The flue gas concentration ranges from 8–15 vol% for typical coal fired plants. Absorption using amines is the currently widely employed commercial technology but there is a significant energy penalty required to regenerate the solvent. Cryogenic distillation is only feasible for CO2 concentrations greater than 90 vol% whereas membranes exhibit low fluxes, degradation, high cost and fouling [7]. Adsorption processes are increasing being used as they tend to utilise less resources and energy and are highly efficient [8–12].

The scope of the present work is to study the adsorption breakthrough characteristics and heat effects of a gas mixture (10% CO2 in 90% N2 by vol) that resembles the concentration of CO2 found in typical dry flue gases and to develop a simple model for the simulation of a non-isothermal adsorption in a fixed bed.
Selection of a suitable adsorbent is one of the important issues in an adsorption process. This adsorbent must possess a high selectivity for CO2 over N2 along with faster uptake rates in order to achieve a higher throughput. The most widely used adsorbents for CO2 removal are zeolites, with 4A, 5A, and 13X being the most popular from this class [13,14], although activated carbon and activated alumina are also used for PSA applications [15,16]. Reynolds et al. [7] used a high temperature PSA with potassium promoted hydrotalcite (HTlc) as adsorbent which exhibited higher capacity at elevated temperatures and good water insensitivity. Attempts have been made to develop and commercialise novel MCM-41 polymer modified molecular basket adsorbents for CO2 removal [17] and amine impregnated pore expanded (PE) MCM-41 adsorbents [4]. Most recently activated alumina composites are being developed in combination with zeolite 13X. The alkaline treated alumina has better resistance against moisture and 13X with a narrow pore size distribution provides a selective adsorptive separation. The adsorbent candidates chosen for this study included Ceca 13X zeolite, Alcan activated alumina AA320-AP and a composite of activated alumina/13X adsorbent, Alcan 650 PCAP.
Pure gas adsorption isotherms for CO₂ and N₂ were measured at 40 and 100 °C for each adsorbent in a constant volume system (Accusorb 2100 Physical Adsorption Analyzer supplied by Micromeritics Instrument Corporation) for Ceca 13X, Alcan AA320-AP and Alcan 650 PCAP. This method involves measuring pressure changes in a known volume of gas exposed to an adsorbent sample. As the gas is adsorbed and allowed to reach equilibrium, the measured decrease in the closed system pressure yields the amount of gas adsorbed under given operating conditions [18]. The pure gas isotherms of CO₂ and N₂ are displayed in Fig. 1a for 13X and AA 320-AP and Fig. 1b for 13X and 650 PCAP. Isotherm data for 13X are repeated in these figures for comparison with other tested adsorbents. The experimentally determined pure gas isotherms have been fitted with the Langmuir model.

From Figs. 1a and 1b, it was observed that the shape of the CO₂ isotherms on 13X was very rectangular whereas the N₂ adsorption isotherms were linear. The initial slope of the CO₂ isotherm is very high when compared to that of N₂ isotherm. This indicates more interactions between CO₂ molecules and the heterogeneous surface of 13X adsorbent. CO₂ favours a more heterogeneous surface due to its higher quadrupole moment compared to N₂. At a lower temperature of 40 °C, the capacities of all tested adsorbents were greater than at 100 °C, as expected, and consistent with always exothermic physical adsorption behaviour. Our previous studies on binary adsorption isotherms of CO₂ and N₂ with 13X zeolite indicated that the binary adsorption behaviour of this pair of gases were completely dominated by the adsorption of CO₂ [19].

13X had a large working capacity for CO₂ when compared to 650PCAP composite and AA320-AP. This observation indicates higher interactions between CO₂ and the more heterogeneous Ceca 13X structure which is highly desirable for the removal of CO₂ from flue gas. A lower column pressure (6.44 atm) was arbitrarily chosen since flue gas is available at low pressures. Operating the column at a much higher pressure would not increase the working capacity for CO₂ since its capacity is levelling off at higher pressures, as can be seen from Fig. 1.

Nitrogen capacities observed were slightly higher for Ceca 13X followed by Alcan 650 PCAP and Alcan 320-AP. Higher N₂ capacities are not desirable for this gas separation since it will be recovered as a product when CO₂ is adsorbed on the adsorbent. When all the above tested adsorbents were compared, Ceca 13X exhibited the larger differences in the adsorption capacities between CO₂ and N₂ at the operating pressure (6.44 atm) and feed concentration (10% CO₂ by vol) at 40 °C. These pure gas isotherm observations suggest that 13X is a suitable adsorbent for the separation of CO₂ in a flue gas application followed by 650 PCAP composite and AA320-AP.

From the literature binary isotherm data, it was observed that 13X adsorbent is a promising adsorbent for CO₂ flue gas separations [19]. Also, the equilibrium phase diagrams obtained for this binary mixture on 13X adsorbent indicated that better separation of CO₂ and N₂ was achieved at high temperatures when compared to 40 °C. This observation also indicates that Ceca 13X is suitable for flue gas separation applications. This finding is similar to the observation made on commercial 13X zeolite by Zhang et al. [3]. 13X was chosen in this investigation as the adsorbent for the lab scale dynamic adsorption unit to study the breakthrough behaviour.

2. Experimental section

A two column dynamic adsorption analysis unit has been designed and built to separate CO₂–N₂ mixtures using zeolite Ceca 13X as the adsorbent supplied by CECA, Honfleur, France. The properties of the adsorbent and the fixed bed are given in Table 1 while Fig. 2 shows a simplified schematic diagram of the apparatus built in-house.

This experimental system was designed to allow easy in situ regeneration of the saturated adsorbent. It primarily consists of the following components: two identical adsorption columns, feed and purge gas, heating tape, an in-line gas heater, a vacuum pump, copper heating/cooling tubes wrapped around the column, solenoid three-way and two-way valves, ¼” and 1/8” outside diameter stainless steel tubing, a data acquisition system, customized control software, thermocouples, a multiposition valve, pressure transducers, mass flow controllers, a mass flow meter, a gas mixing chamber (MC), a gas chromatograph (GC), a non dispersive infrared analyzer (NDIR) and an Edwards high vacuum pump.

Table 1

<table>
<thead>
<tr>
<th>Properties of the adsorbent and fixed bed.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed Length (m)</td>
</tr>
<tr>
<td>Column internal diameter (m)</td>
</tr>
<tr>
<td>Column wall thickness (m)</td>
</tr>
<tr>
<td>Port 1 position (m)</td>
</tr>
<tr>
<td>Port 2 position (m)</td>
</tr>
<tr>
<td>Port 3 position (m)</td>
</tr>
<tr>
<td>Ceca 13X pellet radius (m)</td>
</tr>
<tr>
<td>Ceca 13X bulk density (kg m⁻³)</td>
</tr>
</tbody>
</table>

* Tap location from the column inlet.
The two adsorption columns are made of 316 stainless steel which is known for its corrosion resistance, toughness even at elevated temperatures and for fast heat dissipation. The inside diameter of the column is 4.4 cm, and the length available for the adsorption bed is 61.0 cm. The columns are fitted to inlet and outlet stainless steel conical flow distributors in order to favour plug flow conditions. VCR fittings and Teflon O-rings formed the seals between the column and the flow distributors. One of the columns has three ports that were simultaneously used for temperature and concentration measurements from column centre axis location. These sample ports were connected to a VALCO model SD 32-port micro-electric actuated multiposition valve. This multiposition valve had 32 ports (16 inlet and 16 outlet ports) and had the capability of connecting 16 different sample ports at any time. A 6-port micro-electric actuated injector valve housed the sample gas cell (500 μL) and connected the 32-port micro-electric actuated multiposition valve to a Varian 3400 Series Gas chromatograph (GC) for concentration measurements through 0.32 cm (1/8” outside diameter stainless steel tubing. The sample gas cell within the 6-port micro-electric actuated injector valve was purged with UHP helium for 5 s followed by injecting the CO₂–N₂ gas mixture sample from the desired sample port for a period of 3 s. Each gas sample took 1 min to be analysed in the GC to obtain the CO₂ composition. Therefore, experimental composition data points from the GC were obtained every minute. Since there were three sample location ports along the column, the data point at each sample location was obtained every 3 min. Using a GC provided the flexibility of experimenting with various gases. Disadvantages with the GC included the difficulty in obtaining continuous gas detection at each sample port immediately, as there is a time lag involved with the GC detector. Along with the GC, a non dispersive infrared analyzer (NDIR) was used for continuous CO₂ gas detection (0–20% by vol) at the adsorber column exit. The zero and span drifts were less than ±1% of the full scale. Accurate temperature measurements were obtained by using Omega type-K exposed tip thermocouples.

The two adsorption columns were each equipped with two 590 Barocel pressure transducers at the entrance and the exit of the columns for measuring pressures up to 10 atm with an accuracy of 1% of the reading. The average of the inlet and outlet column pressures was taken as the average column pressure. Due to the low pressure drops (0.26–0.44 kPa) in the range of flow rates studied (4–6.6 SL/min), it represented the true column pressure. A Proportional-Integral-Derivative (PID) controller was built into LABVIEW software (from National Instruments) that was used to control this average column pressure by manipulating column exit mass flow rate via the mass flow controller (MFC) M4. The feed, purge and sample flow rates were controlled by MKS type M100B mass flow controllers (0–10 SL/min) which had an accuracy of 1.5% of the full scale.

The column was fitted with flexible copper coils and a thermostat controlled 50:50 (vol/vol) ethylene glycol–water mixture circulated inside the coils in order to achieve near isothermal conditions for the process. In this study, an attempt is made to replicate a cooling jacket adsorber since it promotes higher adsorption efficiency when compared to beds without jackets [20]. Various components of this system were connected by 0.64 cm (1/4”) outside diameter stainless steel tubing. A data acquisition system in conjunction with LABVIEW...
software from National Instruments was used to collect and record the pressure, temperature, concentration and flow rate data. For the adsorption of carbon dioxide from nitrogen, nitrogen was used both as a feed component and as a purge gas.

At the beginning of the set of experiments used in this study, the adsorption column was isolated from the set up and packed with the Ceca 13X adsorbent. Uniform distribution of the adsorbent pellets inside the column was ensured by continuous tapping of the sides of column. The adsorbent was regenerated in an electric oven at 200 °C under nitrogen flow in order to remove any impurities present in its structure followed by cooling it overnight. Then the two ends of the column (inlet and outlet) were plugged to prevent any leaks and it was connected back to the rest of the experimental set up.

Prior to each run, the NDIR analyzer was calibrated with span gas, UHP N2 and a standard calibrated gas mixture of 10% (by vol) CO2 and 90% (by vol) N2. During pressurisation and after NDIR calibration, the feed gas mixture was prepared in the mixing chamber (MC) filled with glass beads using two pre-calibrated mass flow controllers (MFC) M1 and M2. This gas mixture was sampled through NDIR and GC to establish the variability in concentration. Before each run, the column was pressurised using UHP N2 to the desired column pressure and maintained at the same pressure using the PID controller. During this cycle, N2 is adsorbed by the adsorbent and heat is liberated which raises the temperature within the column to about 55–60 °C. The column was cooled to ambient temperatures (40 °C) using ethylene glycol–water mixture that circulated in the copper coils that surrounded the column. When ambient column temperatures (40 °C) were attained, the adsorption cycle was started by introducing the feed gas mixture (10% CO2 bal. N2) into the column. For each run, the CO2 concentration, flow rates, pressures and temperatures were continuously monitored and the data were recorded in an MS-Excel worksheet.

When the gas concentration at the last sample port reached the feed concentration (10% CO2 bal. N2), the feed flow was stopped. A complete regeneration of the saturated adsorbent was performed by combining high temperature (120 °C) and vacuum in situ, between different experimental runs. During the regeneration cycle, UHP N2 gas was allowed to flow through the column. The completion of this step was verified by stopping the vacuum and analysing the desorbed gas coming out from the column for CO2 concentration using the NDIR analyzer. Complete regeneration of the adsorbent was achieved when the desorbed gas contained no traces of CO2. The column was then allowed to cool under UHP N2 purge. It was then isolated from the rest of the setup by closing the column inlet and the outlet valves.

Prior to the start of the next run, the column was re-pressurised to the desired column pressure and the adsorption cycle was repeated. Adsorption column breakthrough experiments were conducted at a constant adsorption column pressure of 6.44 atm (absolute).

3. Mathematical modelling of the process

The objective of this study was to accurately describe the mass and heat transfer taking place within a packed bed adsorber. The model outlined here describes both the mass and heat transfer in the bulk fluid flowing within the bed, as well as the transport phenomena occurring within the porous solid adsorbent pellets. The model is intended to simultaneously fit three concentration profiles and three temperature profiles at different locations within the packed column. Therefore, the principal assumptions made in the development of the model are as follows:

- Bulk concentration and temperature in the column does not change in radial direction.
- Mass transfer between the surface of the pellet and the fluid is described by a linear driving force model, while the intra-particle mass transfer is described by pore diffusion.
- Within the adsorbent pellets, instantaneous equilibrium is assumed between the mobile fluid phase and the solid surface.
- The adsorption process is non-isothermal. The energy balance accounts for heat generation due to adsorption, heat exchanged with ambient air surrounding the packed adsorber, heat accumulation in the column walls, and the heat accumulation within the pellet and fluid phases.
- Adsorption equilibrium is described by the Langmuir isotherm model.
- Adsorption of nitrogen is considered to be negligible when compared to that of carbon dioxide and that a single component model applies. This assumption is fully justified, since it has been shown in our earlier studies that CO2–N2 binary adsorption behaviour is fully dominated by CO2 with 13X as the adsorbent [19].
- The velocity in the bed changes due to adsorption and heat effects.
- Within the pellet particles, the mobile fluid phase in the pellet void and the solid portion of the pellet are assumed to be locally in thermal equilibrium.
- The adsorbent pellets are assumed to be spheres of homogeneous size, and the adsorption sites are energetically homogeneous.
- Ideal gas law applies.
- The model accounts for two separate populations of pores, each with their respective mass transfer resistances. The two populations of pores represent respectively pores that are easily accessed and those that are accessed with greater difficulty.

3.1. Mass balance equations

Assuming that the bulk concentration of CO2 in the column radial direction is constant, the rate of change in concentration of the flowing gas at any axial position along the column is given by Eq. (1):

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial z} \left( \frac{v \partial C}{\partial z} \right) - \frac{1}{\rho} \frac{\partial}{\partial z} \left( \frac{v \rho}{\rho} \frac{\partial p}{\partial z} \right)$$

The terms on the right hand side of the equation account for the axial dispersion within column, the CO2 transferred from the bulk fluid phase to the adsorbent particles (predicted by the linear driving force model), and the CO2 transferred by convection, respectively.

The mass transfer within the pellet is predicted with a pore diffusion model. CO2 reaching the surface of the solid from the bulk fluid diffuses, according to Eq. (2), along the pores of the pellet due to a concentration gradient. Meanwhile, the concentration of the mobile gas phase within the pores is depleted due to adsorption of CO2 onto the solid surface of the adsorbent pores. It is assumed that the adsorption of CO2 onto the surface of the 13X adsorbent can be considered instantaneous in comparison to the other mass transfer mechanisms [21].

$$\frac{\partial C}{\partial t} = D_m \left( \frac{1}{\rho^2} \frac{\partial}{\partial r} \left( \rho^2 \frac{\partial C}{\partial r} \right) \right) - \frac{1}{\rho} \frac{\partial}{\partial z} \left( \frac{v \rho}{\rho} \frac{\partial p}{\partial z} \right)$$

Eq. (2) was solved twice simultaneously for the two “populations” of pellets (x,y) that represented “easily accessed” (x) and “difficultly accessed” (y) sites. The “easily accessed” sites had the diffusion coefficient, \(D_x\) or \(D_y\), which was calculated using Eq. (3). \(D_y\) represented the “difficultly accessed” sites and was estimated by fitting the model to the experimental data. The
Langmuir isotherm model equation is used to describe the equilibrium that exists between the solid and the gas at a particular temperature. Table 2 gives the list of parameters used in the simulation model of the packed bed adsorber.

### 3.1.1. Mass transfer correlations

The average external mass transfer coefficient between the flowing gas bulk and the pellet, \( k_t \) was calculated using the equation of Wakao and Funakiri [22]:

\[
\text{Sh} = 2.0 + 1.1 \text{(Re}^{0.6} \text{Sc}^{0.33}) \tag{3}
\]

\[ i.e., k_t \frac{D_p}{D_m} = 2.0 + 1.1 \left( \frac{D_p \rho_c \mu_c}{\mu} \right)^{0.6} \left( \frac{\mu_c}{\mu_p \rho_p D_m} \right)^{0.33} \tag{4} \]

The molecular diffusion of CO\(_2\) in N\(_2\) was estimated using the Chapman–Enskog Equation [12]:

\[
D_m = 0.0018583 \sqrt{\frac{T}{P_c}} \left( \frac{M_d}{M_c} + \frac{1}{M_d} \right) \tag{5}
\]

The axial dispersion coefficient was estimated using the following correlation [23].

\[
D_L = 20 + 0.5 \text{Re Sc} \tag{6}
\]

### 3.1.2. Initial and boundary conditions for mass transfer equations

Initially, the packed column adsorber has been regenerated and carbon dioxide is not present such that the fluid and the solid concentrations are zero everywhere within the column:

\[
C_b = C_p = 0, \quad q = 0 \quad t = 0, \quad \forall (r, z) \tag{7}
\]

This initial condition applies for the bulk fluid concentration as well as the concentration in the pellet. “\( r \)” represents both the radial position of the bed and the pellet. Two boundary conditions are required to solve Eq. (1). At the entrance to the column, the feed concentration is known and remains constant throughout the experiment.

\[
C_b = C_{\text{feed}} \text{(i.e., 25 mol/m}^3) \quad z = 0, \quad t \geq 0 \tag{8}
\]

At the exit of the packed bed, it is assumed that the diffusive flux is equal to zero:

\[
\frac{\partial C_b}{\partial z} = 0 \quad z = L, \quad t \geq 0 \tag{9}
\]

To solve Eq. (2), two boundary conditions are required along with the initial condition given by Eq. (7). At the center of the pellet, symmetry prevails whereas at its surface, the rate of diffusion within the pellet must equal the convective mass flux from the bulk fluid.

\[
\frac{\partial C_p}{\partial r} = 0 \quad r = 0, \quad t \geq 0 \tag{10}
\]

\[
-D_m \frac{\partial C_p}{\partial r} = k_t \left( C_b - C_p \right) \frac{\partial r}{r_p}, \quad t \geq 0 \tag{11}
\]

### 3.2. Energy balance equations

The energy balance on the system consists of a balance on the bulk gas phase, a balance on the pellet which is comprised of the solid and the void portions of the pellet, and finally, a balance on the walls of the adsorption column. The energy balance for the bulk gas phase is given by Eq. (12):

\[
\epsilon_c \rho_c C_p \frac{\partial T_{bg}}{\partial t} = k_t \frac{\partial^2 T_{bg}}{\partial z^2} \left( 1 - \epsilon_c \right) h_f \left( \frac{3}{r_p} \left( T_{bg} - T_{bg, z = r_p} \right) - u_c \right) \\
+ \frac{\partial T_{bg}}{\partial z} \left( \frac{\partial r}{r_p} \right) \left( \epsilon_c \rho_c C_p - \frac{4}{r_p} h_t \left( T_{bg} - T_w \right) \right) \tag{12}
\]

This balance accounts for the transfer of energy by axial heat conduction through the bed, energy transfer between the flowing fluid and the surface of the solid adsorbent due to temperature differences, the energy transfer by convection through the bed due to the bulk movement of gas, and finally, the energy transferred to the wall of the column.

#### 3.2.1. Energy balance on the pellet

Eq. (13) accounts for the energy balance on the pellet:

\[
\left[ \epsilon_p \rho_p C_p + \left( 1 - \epsilon_p \right) \rho_c C_p \right] \frac{\partial T_p}{\partial t} = k_p \left( \frac{\partial^2 T_p}{\partial r^2} + \frac{\partial^2 T_p}{\partial z^2} \right) \\
+ \Delta H_{ads} \rho_b \left( \frac{\partial q}{\partial t} \right) \tag{13}
\]

Eq. (13) accounts for both the void and solid portions of the pellet. As was stated previously, the solid and mobile phases within the pellet are assumed to be in thermal equilibrium at a given radial position. The energy balance states that the local rate of change of temperature within the pellets is caused by energy transfer by heat conduction within the pellet and the energy generated within the system due to the exothermic heat of adsorption released when molecules of CO\(_2\) bind to the surface of the adsorbent.

#### 3.2.2. Energy balance on the wall

Eq. (14) represents the energy balance on the column wall [26]. The balance accounts for the heat transfer to the wall from the bulk gas and the heat transfer from the wall to the outside surroundings. The adsorber wall and the coiled coolant tube wall are assumed to be at the same temperature and that the energy balance for the adsorber wall includes the coolant tube wall.
\[
\left[ \frac{d^2 y}{dt^2} \right] - 1 \left[ \frac{d^2 y}{dt^2} \right]^2 = \frac{4}{\rho_w} \left( \frac{\partial T_w}{\partial T} \right) \frac{d^2 y}{dr^2} + \frac{4}{\rho_w} \left( \frac{\partial T_w}{\partial T} \right) h_0(T_w - T_s)
\]

(14)

3.2.3. Initial and Boundary Conditions for heat transfer equations

Initially, the entire column and its contents are at ambient temperature (306 K).

\[
T_{bg} = T_p = T_w = 306 K \quad z = 0, t \geq 0
\]

(15)

Insulation boundary condition is assumed to be valid at the column entrance and exit:

\[
\frac{\partial T_{bg}}{\partial z} = 0 \quad z = 0, L; t \geq 0
\]

(16)

To solve Eq. (13), two boundary conditions are required in the pellet, along with the initial condition given by Eq. (15). At the center of the pellet, symmetry prevails whereas at its surface, the rate of conduction within the pellet must equal the convective heat flux from the bulk fluid.

\[
\frac{\partial T_p}{\partial r} = 0 \quad r = 0, t \geq 0
\]

(17)

\[
-k_p \frac{\partial T_p}{\partial r} = h \left( T_{bg} - T_{p|r=p} \right) r = r_p, t \geq 0
\]

(18)

3.2.4. Heat transfer correlations

Chilton–Colburn analogy [27] was used to estimate the convective heat transfer coefficient for forced convection inside the packed bed:

\[
J_0 = \frac{h_o}{F} = 2.0 + 1.1(Re)^{0.6}(Pr)^{0.33}
\]

(19)

As the experimental conditions represented a laminar flow, Churchill and Chu correlation [28] was used to deduce the average Nusselt number for laminar flow by Eq. (20):

\[
Nu = \frac{h_L}{k_g} = 0.68 + 0.67(\text{Ra} \times \psi)^{0.6}
\]

(20)

\[
\text{Ra} = \frac{\beta \Delta T g L^3}{\nu^2 - Pr}
\]

(21)

\[
\psi = \left[ 1 + \left( \frac{0.492 \nu}{Pr} \right)^{0.4} \right]^{-0.4}
\]

(22)

A two-population adsorbent particle model, representing easily accessible adsorbent sites and those sites which are more difficult to access, was solved. An adsorbent particle normally possesses a wide distribution of pore sizes which for simplicity can be grouped into micro-pores and macro-pores having distinct mass transfer resistances. In this investigation, the model was developed in such a way that the two “populations” were solved in parallel and each one was given a weight representing the percentage of sites which were deemed to be “easily accessed” and “difficultly accessed”. The population weighting factor (FacX) and the diffusion coefficient for the “difficultly accessed” pores, \( D_{ps} \), were determined by fitting the model to the experimental data. When modelling the temperature profile, only a single parameter, the bulk thermal conductivity of the pellet \( k_p \), was used to improve the quality of curve fits. All other parameters were determined either experimentally or calculated using the empirical correlations given in this paper.

This model is intended to provide a simplified approach to representing these two types of adsorption sites within the pellet without having to accurately estimate the radius of the zeolite crystals and the intra-crystalline diffusion resistance within the crystal. Similar systems have been modelled in the literature by including these experimentally determined parameters [29,30].

4. Results and discussions

The scope of this study was the experimental determination of adsorption breakthrough behaviour and heat effects for CO₂–N₂ gas mixture (10% CO₂ by vol in N₂) using the Ceca 13X adsorbent in the laboratory scale set-up. Desorption and estimation of process performance was not a part of this study. Concentration and temperature breakthrough profiles were determined to understand the adsorbent behaviour. The effects of parameters like the omission of the initial cooling step, feed flow rate, and external cooling during the adsorption step were investigated. A novel approach describing two different populations of the adsorbent pellets was used to develop a simple model for the simulation of non-isothermal adsorption in a fixed bed.

4.1. Omission of the initial cooling step

When the thermal regeneration of the adsorption bed is completed, generally a cooling step follows with a purge gas before adsorption step is implemented. This cooling step generally comprises 10–25% of the total cycle time [31]. There is a significant economic advantage if this step could be omitted entirely without affecting the adsorption performance. Basmadjian [31] derived the criterion mentioned below under which the breakthrough time would be independent of the initial bed temperature using equilibrium theory. The criterion is that the ratio of the equilibrium loading to the feed concentration must be larger than the ratio of adsorbent to gas heat capacity and is given by the following inequality [32]:

\[
\left( \frac{q_{ps}}{y_f} \right) > \left( \frac{C_p}{C_{ps}} \right)
\]

(23)

where \( q_{ps} \) is the solid phase adsorbate concentration at the feed conditions, \( y_f \) is the component molar fraction at the feed conditions, \( C_p \) is the solid adsorbent heat capacity and \( C_{ps} \) is the gas phase heat capacity. The second and more important criterion based on adiabatic conditions is given by:

\[
\left( \frac{q_{ps}}{y_f} \right)/(\frac{C_p}{C_{ps}}) > 1.5
\]

(24)

where \( q_{ps} \) is the solid phase adsorbate concentration at the plateau temperature. This temperature, \( T_{pl} \), is obtained from Eq. (25):

\[
T_{pl} = T_f - (q_f \Delta H)/(C_{ps}(q_f/y_f) - C_{ps})
\]

(25)

where \( T_f \) is the inlet feed temperature and \( \Delta H \) is the heat of adsorption. At the beginning of each experimental run, the bed is still hot due to N₂ adsorption during the pressurisation step. However, these criteria were easily fulfilled in this investigation and confirmed by observations during the concentration and temperature breakthrough experiments. The breakthrough times were similar for the experimental runs that were performed while the bed was hot (55–60 °C) and while the bed was at ambient temperature (40 °C). The effect of parameters like low feed concentration (10% CO₂ bal. N₂), high equilibrium loading of the 13X adsorbent (at 0.644 atm partial pressure, \( q = 3.444 \text{ mmol/g} \)), high total system pressure (6.44 atm), and a moderate heat of adsorption (25 kJ/mol) contributed to satisfy this criterion. Therefore, for all the rest of the runs, the initial cooling step was omitted at the beginning of the adsorption cycle.

It was observed that these criteria contributed to the slow movement of the adsorbate concentration front thus allowing the temperature wave to pass ahead. An interesting observation to note was the viable option of using thermocouples only to detect breakthrough behaviour under similar conditions, without the use of sample gas concentration detectors. This is possible for bulk gas separations that exhibit a higher heat of adsorption.
4.2. Effect of feed flow rate

Fig. 3 gives the concentration breakthrough curves obtained for CO$_2$ adsorption from a CO$_2$/N$_2$ mixture (10% CO$_2$ bal. N$_2$) on a packed bed of 13X for two different flow rates to see the effect of the feed flow rate at a constant adsorption pressure of 6.44 atm (absolute). The plot gives the concentration of CO$_2$ in the gas phase as a function of time at the column outlet. A Non-Dispersive Infrared (NDIR) analyzer was used at the column exit to obtain continuous gas concentration measurements. It was observed that a higher feed flow rate of 6.6 SL/min contributed to an early breakthrough since the bed got saturated faster with more CO$_2$ going through the column compared to a lower feed flow rate of 4 SL/min. For 6.6 SL/min, the mass transfer zone moved quicker and mass transfer coefficient was higher because of the higher Reynolds number.

Tailing was seen towards the bed exit for both flow rates. This is an indication of the slow intra-particle diffusion within micro pores of the adsorbent, presence of non homogeneous particles and varying flow patterns.

4.3. Effect of external cooling

Fig. 4 gives the concentration breakthrough curves obtained with and without cooling for CO$_2$ adsorption from a CO$_2$/N$_2$ mixture (10% CO$_2$ bal. N$_2$) on a packed bed of 13X at two different flow rates to see the effect of external cooling at a constant adsorption pressure of 6.44 atm (absolute). The plot gives the concentration of CO$_2$ in the gas phase as a function of time at the column outlet. During the adsorption step, a mixture of 50:50 (by vol) ethylene glycol and water was circulated as a coolant (at 0 °C) in the copper coils that surround the column. Although this would lead to an increase in the energy consumption, the objective of these runs was to operate the column at the lowest coolant temperature possible (which was 0 °C) and study the breakthrough behaviour at a constant column pressure of 6.44 atm (absolute). For identical feed flow rates, it was observed that the cooling effect made the breakthrough curves steeper, decreasing the mass transfer zone. Since physical adsorption is exothermic, lower column temperatures contributed to an increase in the capacity of Ceca 13X adsorbent and, as a result, led to a delayed concentration breakthrough when compared to ambient non-isothermal operations.

Apart from studying the concentration breakthrough behaviour using an NDIR analyzer, thermocouples were located at different sample ports (at positions 10.2, 30.5 and 50.7 cm from column inlet) to study the temperature breakthrough behaviour. The heat of adsorption basically dictates the type of adsorbent regeneration conditions that have to be employed. A higher heat of adsorption requires high temperature and/or lower pressures during regeneration.

Fig. 5a gives the temperature breakthrough curves obtained for CO$_2$ adsorption from a CO$_2$/N$_2$ mixture (10% CO$_2$ bal. N$_2$) in a packed bed of Ceca 13X at 4 SL/min to see the effect of external cooling during adsorption step at a constant adsorption pressure of 6.44 atm (absolute). The plot gives the temperatures of the column at different positions as a function of time. The higher heat of adsorption observed for CO$_2$ on Ceca 13X (25 kJ/mol) contributed to reach a temperature of about 117 °C when the column was at room temperature, as observed in Fig. 5a. Although more heat was released during the experiments with cooling due to higher capacities at low temperatures, the presence of the coolant resulted in a lower peak temperature (around 98 °C). The temperature rise in port #1 (at 10.2 cm from column inlet) was smaller when compared to the ports (#2, #3) closer to the column exit. When the feed gas is introduced, adsorption begins to take place within a narrow mass transfer zone at the entrance of the column. The energy that is released due to adsorption, heats the adsorbent particles as well as the gas within the bed and the column walls near the entrance of the column. Some of the energy that is released will be transferred through convection and axial heat diffusion which begins to warm the downstream column contents. By the time the mass transfer zone has moved down the bed to the downstream sampling ports, the adsorbent particles have already been heated partially due to the energy carried from the upstream sections of the bed due to convection. The heat losses at the end section of the small size adsorber bed also contribute to higher temperatures observed for the second and third peaks. High heat losses are representative of lab scale adsorbers when compared to industrial size adsorbers since they would have a high surface area for heat loss to volume ratio [33]. When energy is released due to adsorption in this section of the bed, a higher peak is attained. This release of energy that is carried along the length of the column also explains the presence of tailing particularly for the experiments in which no cooling is present. When cooling is conducted, less tailing is evident. The coolant provides a higher driving force for energy transfer through the walls of the column due to a larger temperature gradient as opposed to along the length of the column.

Similar results were obtained for a higher feed flow rate of 6.6 SL/min as observed in Fig. 5b. Temperatures obtained were higher for 6.6 SL/min run, since the quantity of CO$_2$ being fed into
the column was greater than at 4 SL/min (Fig. 5a). A higher feed flow also signified a larger Reynolds number and thus a higher mass transfer coefficient which resulted in faster adsorption and thus a higher temperature.

4.4. Modelling

For an experimental feed flow rate of 6.6 SL/min, a constant column pressure of 6.44 atm (absolute) and a feed composition of 10% CO₂ and 90% N₂, samples were obtained at three different positions along the length of the packed column and analysed for their composition by a gas chromatograph (GC) by using the multiposition valve. The experimental concentration vs. time plots obtained for different positions in the column are given in Fig. 6 and compared to the same plots from modelling. This figure clearly shows that the experimental data are very well represented by the two-population model at all three ports for the duration of the experiment.

The experimental data display a significant amount of “tailing” when the feed concentration is approached. Tailing is a common observation in breakthrough experiment in liquid and gas systems [34]. Within the porous adsorbent pellets, there exists a distribution of pores ranging from micro-pores to macro-pores. Typically, the macro-pores which are larger in size are the first to fill with the adsorbate feed gas. The micro-pores which are smaller in diameter tend to fill at slower rates. This difference in the rate of diffusion causes a proportion of the adsorbent sites to remain unsaturated while the other proportion of easily accessed sites saturates quicker. Due to the slower rate at which the pores get saturated, also, since most of adsorption uptake happens in the smaller pores, the width of the mass transfer zone is extended causing the “tailing” characteristics observed in many adsorption systems.

The two-population adsorbent pellet model appears to adequately describe the tailing that is present in the experimental data. The proposed model is considerably less complex in terms of computational resources required to solve the system of differential equations and the type of experiments which are required to determine the intra-crystalline diffusivity.

The temperature changes in the column were also obtained by taking temperature measurements using thermocouples at the same three positions along the length of the packed bed as the concentration measurements. For the experimental conditions of 6.6 SL/min feed flow rate, a constant column pressure of 6.44 atm (absolute) and a feed composition of 10% CO₂ and 90% N₂, the temperature changes measured at three ports in the column along with the predicted model fits are displayed in Fig. 7.

The model predicts the breakthrough time associated with the sharp temperature rise at each port very well. However, the amplitude and the curvature of the temperature changes were not
matched exactly. This observed deviation may be caused by use of a constant heat of adsorption for CO2 in the model and common gas adsorption systems [24,35–37].

Fig. 8 combines the plots of concentration breakthrough (from Fig. 6) and temperature breakthrough profiles (from Fig. 7) along the length of the column. Temperature and concentration measurements were performed at the same location in the column. Since there were three different ports, measurements were done at three different positions along the length of the column. This figure clearly shows that the temperature front moves slightly ahead of the concentration front, while concentration breakthrough is observed approximately at the peak of the temperature as the feed gas moves from the column inlet to the outlet.

This observation is very significant since it suggests that concentration breakthrough in a column could be easily detected by using thermocouples only. In the case of gas mixtures that exhibit significant heat effects, thermocouples can be used as an indirect method of predicting the concentration breakthrough. An expensive concentration measurement device would not be needed. Similar behaviour was observed for the experimental run with the feed flow rate of 4 SL/min.

By establishing a model which can predict the mass and heat transfer within the fixed bed, we have shown that we can depend on the movement of heat transfer zone in our application and use this to infer about the state of the composition within the packed bed adsorber.

5. Conclusions

1. Heat effects are significant for a bulk carbon dioxide separation from a gas mixture of 10% CO2 (by vol) in N2 using Ceca 13X adsorbent.
2. The breakthrough time of Ceca 13X adsorbent is independent of the initial bed temperature resulting in a significant economic advantage without affecting the adsorption performance.
3. An earlier breakthrough time was observed for a higher feed flow rate of 6.6 SL/min compared to 4 SL/min.
4. Cooling during the adsorption cycle decreases the mass transfer zone and leads to a longer breakthrough time.
5. By using the two population model, the curvature of the concentration breakthrough curve including the noted tailing was predicted with good accuracy.
6. The prediction of the energy profile was less accurate by the model. However, the point at which the temperature breakthrough occurs is estimated with good accuracy which is the most important factor for industrial applications.
7. Using online measurements of temperature in the column bed, can predict the concentration breakthrough for mixtures and adsorbents exhibiting high heat effects.

Acknowledgements

Financial supports received from Ontario Centres of Excellence (OCE), RioTinto Alcan and Air Products & Chemicals Inc., are gratefully acknowledged.

References


