

Measurement of CO₂ adsorption using the cost-effective dynamic column breakthrough method

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The adsorption of carbon dioxide (CO₂) on solid sorbents or any gas adsorption in general can be experimentally determined using various techniques. The present study demonstrates a dynamic column breakthrough method for the measurement of CO₂ adsorption using a cost-effective purpose-built single-column fixed-bed adsorption unit. The CO₂ adsorption capacity is estimated using a graphical method that does not require knowledge of the variation of molar CO₂ flow rate at the column exit. The experimental method is validated using a commercial zeolite 13X adsorbent.

Keywords: Carbon dioxide adsorption, dynamic column breakthrough method, gas chromatography, zeolite and sorbent.

CARBON DIOXIDE (CO₂) capture and storage (CCS) is a mid-term commercially viable technological option to reduce anthropogenic greenhouse gas (GHG) emissions and best applied to large point sources, including fossil-fuel power plants, fuel processing plants, and industrial plants (iron and steel, cement and petrochemicals). CO₂ capture, its transportation and storage are the three main steps in CCS technology¹. Among these, CO₂ capture is very expensive and hence considered the most critical step. CO₂ can be captured using different techniques, including absorption, membranes, cryogenic distillation systems and adsorption². In recent years, CO₂ adsorption onto solid sorbents has been widely studied as an alternative to benchmark absorption technology. The selection of a suitable CO₂ adsorbent is a daunting task. An ideal adsorbent must possess many characteristic properties, including high working capacity, high selectivity, low regeneration energy and fast reaction kinetics. Among

these, high adsorption capacity is the paramount desirable property³⁻⁷.

Different methods can be employed to experimentally determine the CO₂ adsorption capacity of an adsorbent. The literature reports numerous techniques for gas sorption measurement under various conditions. While volumetry/manometry and gravimetry are the most popular classical techniques, recent techniques include oscillometry, calorimetry and impedance spectroscopy. In addition, temperature programmed desorption flow method, gas chromatography, zero length column (ZLC) method, fixed-bed reactor and fluidized-bed reactor also have been explored using either pure gas and multicomponent gas. In fact, huge numbers of gas sorption analysers with a variety of techniques are available in the market today. For example, there are several commercial, highly precise instruments for conventional measurement techniques such as volumetry and gravimetry. However, these are rather expensive and provide accurate information about adsorption capacity on equilibrium basis only. Even though the adsorption equilibrium data are necessary for sorbent selection, in practical operations it is not feasible to utilize the maximum capacity of adsorbent completely due to transfer effects involved in actual fluid–solid contacting processes⁸. Typically, the solid sorbents are employed in cyclic processes of adsorption and desorption. Evaluation of material characteristics under dynamic regime of operation is important to ascertain the extent to which the equilibrium uptake may be translated into breakthrough capacity⁹.

In the light of these prospects, the present communication demonstrates a dynamic column breakthrough (DCB) method for the measurement of CO₂ adsorption using a cost-effective purpose-built single-column fixed-bed adsorption unit. Apart from cost-effectiveness, this method presents other advantages such as speed and flexibility over conventional gravimetric or volumetric methods. Further, the DCB method provides information about adsorbent performance under process conditions, allowing the validation of numerical models for process simulations¹⁰.

Additionally, more representative data can be obtained as a large amount of adsorbent is required for analysis¹¹.

Figure 1 is a schematic of the purpose-built single-column fixed-bed adsorption unit. The experimental set-up mainly consists of three sections: a gas manifold system, a fixed-bed reactor, and a gas measurement system.

The first section consists of a mixed gas cylinder (10 vol% CO₂ + 90 vol% He), an ultrapure helium cylinder, and an ultrapure N₂ cylinder. These gas cylinders were supplied from a certified local gas agency. All cylinders are fitted with two-stage pressure regulators. The regulators can accept the pressurized gas up to 275 bar and deliver it in the pressure range 0–15 bar. These regulators require less readjustment and the gas can be delivered at a

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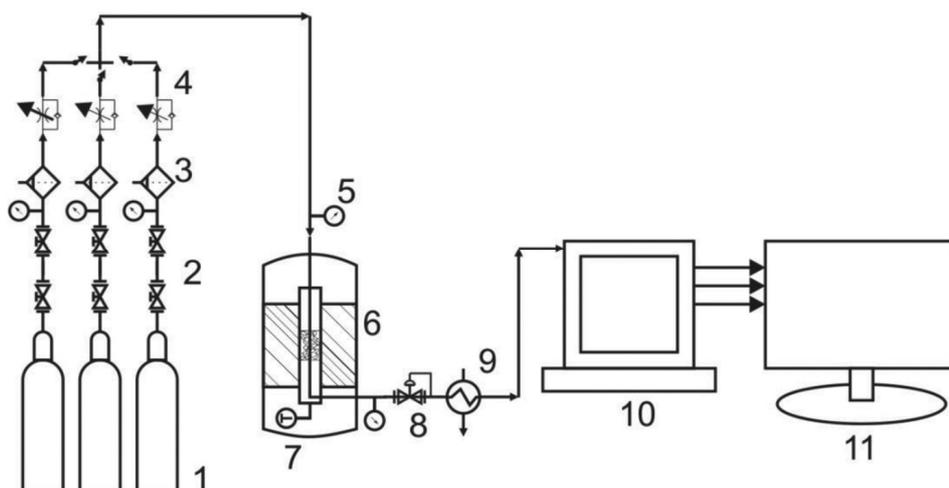


Figure 1. Experimental set-up. 1, Cylinders; 2, Two-stage pressure regulators; 3, Gas clean filter system; 4, Differential flow controllers; 5, Pressure sensor; 6, Reactor bed; 7, Electric furnace; 8, Back-pressure regulator; 9, Heat exchanger; 10, Gas chromatograph; 11, Personal computer.

constant pressure despite variation in the inlet pressure. The cylinders are connected to a gas clean filter system and subsequently, to a flow-control unit using stainless steel (grade 316) tubes having 3.2 mm outer diameter via toggle valves. The flow control unit consists of three differential flow controllers (VCD-1000, Porter Instrument Division, Parker, USA) with a digital flow display. The gas flow can be controlled in the range between 1 and 110 ml min⁻¹. These controllers demonstrate an accuracy of 1% full scale and have been calibrated for corresponding gases using a borosilicate glass soap-film flow meter.

The second section mainly consists of a fixed-bed reactor and an electric furnace. The fixed-bed column is made of stainless steel (grade 316) with a total length of 320 mm and an internal diameter of 10 mm. It is equipped with a porous circular disk located at about 100 mm from the base of the column. Another stainless steel tube of the same grade with 3 mm thickness and 5 mm internal diameter is placed just below the porous circular disk in order to minimize the dead volume. The reactor is positioned vertically inside in an temperature programmable electric furnace (225 mm length × 180 mm width × 250 mm height) made up of powder-coated mild steel sheet. The furnace consists of a ceramic tube (20 mm internal diameter, 240 mm length) with an electrical resistor (0.8 kW, 230 V) coiled around, inside the thermal insulation jacket. The ends of the reactor are extended out of the furnace and are much cooler than the experimental temperature maintained in the central zone of the furnace. A K-type thermocouple is inserted from the column exit in such a way that there is gap of about 1 mm between the tip of thermocouple and porous circular disk. The thermocouple is connected to a PID controller (ESM-4450, EMKO Elektronik, Turkey) and used to monitor the column temperature continuously with an

accuracy of ±1°C. Thus, the furnace is used to heat the reactor to the desired temperature in the range from ambient to 1000°C. The reactor is connected to other sections of the experimental set-up using stainless steel (grade 316) tubes having 1.6 mm outer diameter to minimize the dead volume. Further, the reactor is equipped with two pressure transducers (Model-100, Chemlabs, India) at the entrance and the exit of the reactor. These are used to monitor the pressure and calculate the pressure drop. They are capable of measuring pressures up to 10 bar with an accuracy and resolution of 0.007 bar. The pressure inside the reactor is controlled by means of a fine control valve, located in the outlet pipe, resulting in back pressure in the desired range, i.e. 1.0–6.0 bar. An additional provision is made for cooling the column effluent using a heat exchanger in case of above ambient temperature adsorption.

The third section is the gas measurement system. It consists of a six-port sampling valve and a gas chromatograph (1100, Mayura Analytical Pvt Ltd, Bengaluru). The gas chromatograph is mainly equipped with a stainless steel packed column (80/100 Porapak Q), a thermal conductivity detector (TCD) detector, a data station and a hydrogen gas generator. The TCD is made up of four dual-path tungsten–rhenium filaments (32 Ω individual resistance; GOW-MAC, USA), capable of operating in the temperature range of 5°C above ambient to 450°C (accuracy ±0.2°C) with a sensitivity better than 10 ppm O₂. The hydrogen generator (Model H2-I, Chemlabs) is a portable stand-alone system, capable of producing ultrapure H₂ (99.9995%) at a maximum pressure of 4 bar in the flow range 0–300 ml min⁻¹.

Prior to the experiment, the TCD signal was calibrated by injecting known volumes of CO₂. The TCD signal was found to be linear. In a typical experiment, a known

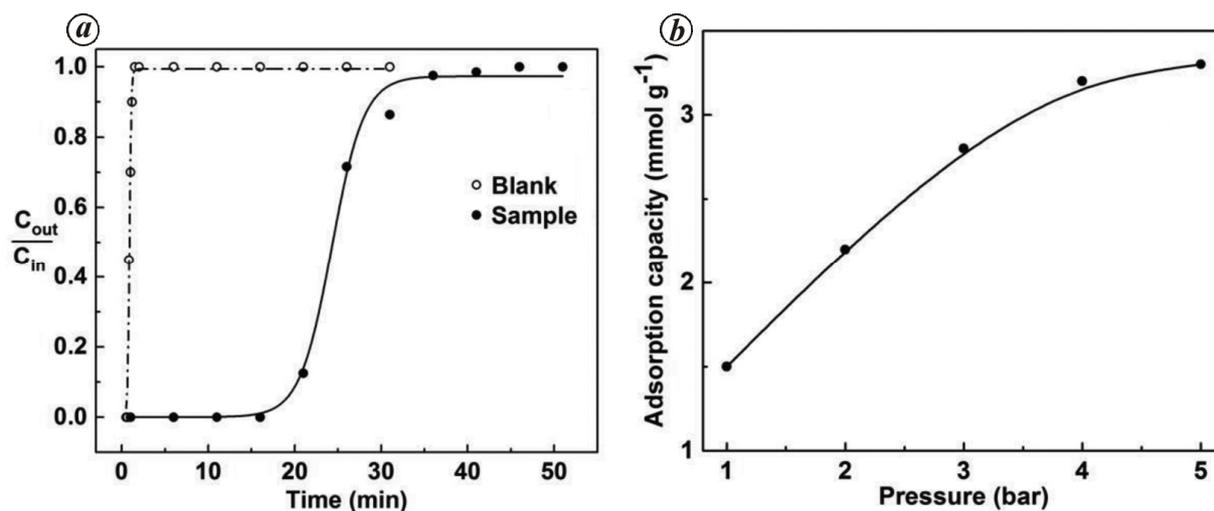


Figure 2. *a*, Typical breakthrough curve for CO₂ adsorption on zeolite 13X and blank run. *b*, CO₂ adsorption isotherm on zeolite 13X.

amount of adsorbent is loaded into the middle of column, where a layer of ceramic wool supported onto the porous circular disk prevents the adsorbent particles from falling down. The sample loading in the middle portion of column ensures the favourable pre-heat of the incoming gas flow. The remaining upper portion of the column is packed with ceramic wool. The loading of sample in this way ensures retention of packing in position, reduction of dead space, prevention of loss of adsorbent due to gas flow, and prevention of heat loss from the column ends. After mounting the column, the gas leak test was carried out using a soap-film flow meter. Then, the sample was pre-treated at a desired temperature for a known period with N₂ flowing at a rate of 30 ml min⁻¹, followed by cooling to adsorption temperature. The stable flow of working gas (10% CO₂ balanced by helium) in the desired range was then established with reactor bypass. The run was initiated by switching from nitrogen flow to working gas flow. Then, a portion of column effluent gas was fed to the gas chromatograph to monitor CO₂ concentration. After attaining saturation, the sample was flushed with N₂ for a known period and proceeded for desorption at the desired temperature. The adsorption and desorption can be continued to obtain the multicycle stability of adsorbent. The experiment was repeated at least twice for the first adsorption capacity to ascertain the reproducibility of results. Blank experiment was performed by replacing the adsorbent material with a non-adsorbing material (quartz sand), having similar particle size range and bed volume as that of the active material.

The experimental isobaric CO₂ adsorption curve in the DCB method gives the apparent CO₂ adsorption capacity. This includes the actual amount of CO₂ adsorbed onto the adsorbent as well as the amount of CO₂ accumulated in the dead volume of the adsorption unit, voids in the

packed bed, and inter-granular space. Hence, if q denotes the amount of CO₂ adsorbed/accumulated, then

$$q_{\text{measured}} = q_{\text{sorbent}} + q_{\text{dead space}} + q_{\text{bed porosity}} + q_{\text{pore}} \quad (1)$$

If the adsorbent is in the powdered form, q_{pore} can be neglected. The dead space corresponds to the void space in column, piping and on-off valves. This does not show any considerable change with the varying operating conditions. The dead space has been reduced to a minimum through proper design of the experimental set-up as explained earlier in the text. Further, the sum of $q_{\text{dead space}}$ and $q_{\text{bed porosity}}$ can be estimated using a blank experiment.

The actual adsorption capacity of an adsorbent (q_A) in terms of mmol of CO₂ per gram of adsorbent is calculated using the equation

$$q_A = \frac{F \times C_{\text{in}}}{\rho_p \times V_S \times 22.4} \left[\left(\int_0^t \left(1 - \frac{C_{\text{out}}}{C_{\text{in}}} \right) dt \right)_{\text{Sample}} \right] - \left[\left(\int_0^t \left(1 - \frac{C_{\text{out}}}{C_{\text{in}}} \right) dt \right)_{\text{Blank}} \right] \quad (2)$$

where F is the feed flow rate (normal, ml min⁻¹), ρ_p the packing density of adsorbent (g cm⁻³), V_S the packing volume of adsorbent in the adsorber (cm³), and 22.4 is the conversion factor (ml mmol⁻¹). C_{in} and C_{out} are the influent and effluent CO₂ concentrations (vol%). The integral term (min) in eq. (2) can be easily obtained by a graphical method using the plot of $(1 - (C_{\text{out}}/C_{\text{in}}))$ versus time. This methodology does not require knowledge of the variation of molar CO₂ flow rate at the column exit. It simply allows one to calculate the total mass retained by the column as a percentage of the total mass that entered the

system. Further, q_A can be expressed in two different terms. The term q_{SAC} refers to saturation adsorption capacity and is calculated by integrating the eq. (2) from $t=0$ to saturation time (t_s), when C_{out} reaches C_{in} . The term q_{BT} refers to breakthrough capacity of the adsorbent and is calculated by integrating eq. (2) from $t=0$ to breakthrough time (t_b), when C_{out} reaches 10% of C_{in} (refs 12, 13). In the present study, the saturation time for blank run with 2 g of sample at a gas flow rate of 30 ml min^{-1} was found to be 1.5 min. This corresponds to $2.3 \text{ ml of CO}_2/\text{g}$ or $0.106 \text{ mmol of CO}_2/\text{g}$, which is the minimum adsorption that can be detected.

In order to validate the experimental method, commercial zeolite 13X (Sorbead, India) was studied for CO_2 adsorption at room temperature in the pressure range of 1–5 bar. Figure 2a shows a typical graph of breakthrough curve for CO_2 adsorption on zeolite 13X and blank run. Figure 2b shows the CO_2 adsorption isotherm on zeolite 13X. In all cases, the ratio of $\text{Area}_{\text{blank}}/\text{Area}_{\text{sample}}$, obtained from the graphical method, was found to be less than 4.8%. This value being less than the allowable 5% indicates that a pair of sample run and blank run at any operating condition employed in the present study is sufficient to yield a reasonable estimation on the system error¹⁴. In the present study, the CO_2 adsorption capacity of zeolite 13X at 25°C under a total pressure of 1 bar was found to be 1.5 mmol g^{-1} . The value of adsorption capacity in the range 1.25 to 2.1 mmol g^{-1} has been reported in the literature under somewhat similar test conditions and the method of measurement^{15–18}. This implies the validity of the experimental method and analysis carried out in the present study.

The adsorption of CO_2 on solid sorbents or any gas adsorption in general can be experimentally determined using various techniques. The present study demonstrates the DCB method for measurement of CO_2 adsorption using a cost-effective purpose-built single-column fixed-bed adsorption unit. With a proper design, it has been shown that a pair of sample run and blank run at any operating condition employed in the present study is sufficient to yield a reasonable estimation on system error. The calculation of adsorption capacity using the graphical method was found to be simple and effective. The experimental method has been validated using a commercial zeolite 13X adsorbent.

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