



Adsorption of carbon dioxide by diethanolamine activated alumina beads in a fixed bed

M. Auta^{a,b}, B.H. Hameed^{a,*}

^a School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

^b Department of Chemical Engineering, Federal University of Technology, Minna, Nigeria

HIGHLIGHTS

- Activated alumina was functionalized with 0.8 M diethanolamine (DAAB).
- Physical and chemical characterizations of the adsorbents were carried out.
- Fixed-bed column adsorption of carbon dioxide from the gas mixture (CO₂/N₂).
- Multi-cycles adsorption tests of carbon dioxide.

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ABSTRACT

Application of mesoporous activated alumina functionalized with diethanolamine (DAAB) for selective adsorption of carbon dioxide (CO₂) from its mixture with nitrogen gas was investigated. Morphological structure, elemental composition and the functional groups present in the DAAB were analyzed using the scanning electron microscopy; energy dispersive X-ray technique and Fourier transform infrared analysis. Investigation of effect of the gas mixture feed flow rate, column adsorption temperature, DAAB bed height and concentration of CO₂ in the feed stream revealed that 90 mL/min, 35 °C, 3 g and 10% of CO₂, respectively were the optimum operating conditions for the highest adsorption capacity of 55.94 mg/g. The DAAB multi-cycle CO₂ adsorption test revealed that it can be reused successfully for about 13 times with high sorption capacity. The DAAB is a promising adsorbent that can be used to capture CO₂ pollutant molecules.

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1. Introduction

An easy to use, regenerate, multi-cycle and high adsorption capacity adsorbent is the yening for global community in curbing carbon dioxide environmental pollution [1]. This is feasible by monitoring the physical (surface area and porosity) and chemical properties of adsorbent during preparation [2]. The acidic CO₂ adsorption is favorable on basic surfaces or surfaces of adsorbents with insignificant acidic characteristics [3,4].

Increasing basic functionality of adsorbents can be carried out through: modification of surface oxygen functionalities [5], adsorbent basal planes [6], functionalities with nitrogen containing compounds (NH₃, amines etc.), decomposition of surface acidic functional groups through calcinations [7]. Amine modification of adsorbents for capturing CO₂ is a promising way of evacuating it

from flue gases [8,9]. Amine modified adsorbents has high selective adsorption and high rate of diffusion of the CO₂ within the mesopores [10,11]. The modified (amine) adsorbent ability to promote CO₂ adsorption from both flue gas and ambient air also depends on the method (wet impregnation, grafting or insitu polymerization) of the amine monomers immobilization [11]. This is additional to microporous, large pore volume and surface area of adsorbents that promotes physical adsorption of CO₂. Various mesoporous materials such as activated carbons, alumina, silica (MCM-22, MCM-36, MCM-41, MCM-42, SBA-15, SBA-16 etc.) have been modified with amine compounds for CO₂ adsorption. Principally, impregnation and grafting are the two major methods employed for mesoporous adsorbents modification with amine compounds. The later involves interaction of amine molecules with surface hydroxyl group while the former method involves attachment of amine molecules to the mesoporous surface by van der Waals forces [12].

Monoethanol amine is among the commonest solvents used for CO₂ capturing but it requires energy for regeneration and also

* Corresponding author. Fax: +60 45941013.

E-mail address: chbassim@usm.my (B.H. Hameed).

causes corrosion [5,10]. Despite these limitations, enhancement of effective adsorption and lowering of carbamate (product of CO₂ adsorption on amine reaction (CO₂ + 2R-NH₂ = R-NHCOO- + R-NH₃⁺)) formation is promoted by the use of the amines (sterically hindered) with bulky substituent lying near. A high mesoporous material with suitable amine group can yield an excellent CO₂ adsorbent [13].

The readily available, cheap, mechanically stable, amphoteric, mesoporous and transitional nature of alumina has been utilized for adsorption purposes [13,14]. Despite the mesoporous alumina inherent ability, its modification with amine for CO₂ adsorption reports is limited in literature [13,15,16].

In this study, mesoporous activated alumina was synthesized with diethanolamine through impregnation for adsorption of CO₂ in a fixed bed column. The relationship between the resulting breakthrough curves of the CO₂ adsorption on the DAAB adsorbent and the adsorption parameters (temperature, concentration, flow rate, bed height, CO₂ %) were evaluated. Regeneration and multi-cycle use of the DAAB adsorbent was investigated.

2. Materials and methods

2.1. Materials

Diethanolamine (2,2'-iminodiethanol, Bis(2 hydroxyethyl) amine) and methanol were supplied by Sigma-Aldrich; activated alumina beads was purchased from OMI(M) SDN. BHD., all in Malaysia. High purity carbon dioxide (99.9%) and nitrogen (99.9%) gases were obtained from Well gas company Malaysia.

2.2. Preparation of CO₂ adsorbent

Activated alumina beads were sieved into different particle sizes (500 μm⁻¹ mm, 1–2 mm, 2–3 mm) and dried under vacuum (70 °C) for 6 h after washing with distilled water. The dried different particle sizes beads were used as plain activated alumina (PAA) adsorbent.

Ten grams (10 g) of the prepared PAA was added to 300 mL of 0.8 M diethanolamine (23 mL of diethanolamine plus 277 mL of methanol) and stirred for 5 h at room temperature. The mixture was filtered and washed with methanol and then dried under vacuum at 70 °C for 6 h. The dried activated alumina beads functionalized with diethanolamine (DAAB) were packaged in air tight container for further use.

2.3. Fixed-bed column adsorption

The DAAB adsorbent was preheated for drying in an inert (under constant nitrogen flow) fixed-bed column (42 cm length and 1.1 cm diameter) at 110 °C for 1 h and then cooled to the desired adsorption temperature. In an upward flow pattern, a mixture of carbon dioxide (10% CO₂) and nitrogen (balance of CO₂ v/v) of 99.99% purity each was passed through the adsorption column via an AALBORG (model AFC26 NY, USA) calibrated mass flow controller. An online carbon dioxide analyzer 906 (Quentek instrument, USA) model was used to determine the residual CO₂ in the fixed-bed column adsorption effluent after every 10 s.

Effect of adsorption parameters such as gas influent flow rate (90, 120 and 150 mL/min), percentage of CO₂ in the feed (10, 15, and 20%), amount of adsorbent (DAAB) (2, 3 and 4 g) in the fixed-bed and adsorption column temperature (35, 45 and 55 °C) on the CO₂ adsorption in the fixed-bed column were studied. The column adsorption temperature range selected covers a typical post flue gas desulfurization range of 45–55 °C [17].

2.4. Regeneration of adsorbent

The CO₂ adsorbed on 3 g (1–2 mm size) DAAB at 35 °C of 10% CO₂ influent concentration in the feed flow rate of 90 mL/min was desorbed by raising the column temperature to 110 °C for 1 h under flow of nitrogen gas. A complete desorption was marked by constant residual CO₂ in the exit column effluent determined through the carbon dioxide analyzer. The fixed DAAB in the column was reused for cycles of adsorption as in section 2.3 after purging the trapped gas with a vacuum pump for 30 min.

2.5. Characterization of adsorbent

Nitrogen adsorption–desorption of the DAAB operating with static volumetric technique using an autosorb Brunauer–Emmett–Teller Micrometric (BET) ASAP 2020 was used to determine the BET surface area and porosity. The DAAB sample was first degassed at 300 °C for 2 h to measure the equilibrium pressure of the known volume of liquid nitrogen for the isotherms generation. Then the Barrett–Joyner–Halenda (BJH) and t-plot method evaluation of the average pore size distribution and total pore volume were used, respectively.

The morphological structure and elemental composition of the DAAB were determined using an integrated scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) microanalysis (Oxford INCA 400, Germany).

Chemical functional groups on the DAAB surface before and after adsorption of CO₂ were quantitatively identified using Fourier transform infrared spectroscopy (FTIR) analysis. Potassium bromide (KBr) and the DAAB were mixed in a 20:1 ratio to prepare a 7 mm diameter disc (1 mm thick) using hydraulic press technique. An observable transmission spectrum of the sample was recorded between 4000 and 400 cm⁻¹ after 100 scans with the aid of an FTIR Thermo Scientific model IS10 Nicolet spectrometer, U.S.A.

3. Results and discussion

3.1. Characterization of DAAB adsorbent

The morphological and elemental composition of the activated alumina functionalized with diethanolamine adsorbent (DAAB) is shown in Fig. 1. Amorphous and some platelet morphology exhibited by bayerite structure of the plain activated alumina SEM reported in our previous research [18] were traceable in the modified DAAB adsorbent (Fig. 1). This is similar to SEM analysis of acid modified alumina adsorbent as-synthesized diethylmalonate treated mesoporous alumina [14,19]. Presence of peaks of some carbon and nitrogen molecules revealed that successful functionalization of the activated alumina was carried out when compared with the plain activated alumina elemental composition result reported in our previous work [18].

Blockages of pore width of activated alumina were observed after functionalization with diethanolamine. The BET textural analysis revealed a pore size and surface area of 5.3 nm and 205 m²/g for DAAB as compared with 5.7 nm and 207 m²/g, respectively of the plain activated alumina reported in our previous work [18]. The decrease in surface area of DAAB is similar to observation made with polyethylenimine-impregnated mesoporous alumina sorbent prepared for CO₂ adsorption [14]. However, a total pore volume of 0.39 nm for DAAB was obtained which showed an enhancement after functionalization. Dissolution of the DAAB wall during functionalization may have caused the expansion or structural changes due to reaction between the diethanolamine and the alumina which is similar to observation made during N-(triethoxysilylpropyl) ethylenediaminetriacetic acid modification of SBA-15

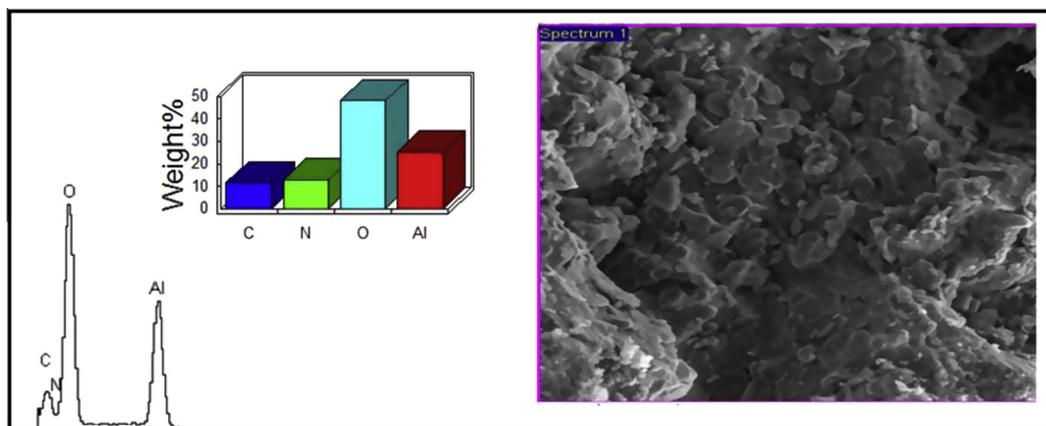


Fig. 1. Elemental composition and morphological structure of the DAAB.

silica [20]. The effect of amine functionalization of the activated alumina further affirmed that adsorption of the CO_2 may not solely have been by single phenomenon but through mass transfer or chemical or physical or combination of the adsorption processes [6,21].

The FTIR spectrums of diethanolamine functionalized activated alumina before adsorption (DAAB) and after adsorption (DAABU) for CO_2 capturing have some symmetrical functional groups peaks; the spectrums are presented in Fig. 2. The symmetrical peaks were found around $3200\text{--}3500\text{ cm}^{-1}$, at 1647 cm^{-1} and 1384 cm^{-1} signifying stretches of O–H or N–H groups, some amide (N–H) group peaks and presence of C–H and C–N groups [22]. The less pronounced peaks at 1647 cm^{-1} and between 3200 and 3500 cm^{-1} on the DAABU spectrum were attributed to the adsorbed CO_2 molecules on its surface which led to extinction of some of the functional groups. Vibration of primary amine NH_2 wag was observed between the DAAB (625 cm^{-1}) and DAABU (610 cm^{-1}). This was due to lowering of the carbamate stability formed from the adsorption of the CO_2 with the amine functionalized activated alumina adsorbent thus promoting effective adsorption of the pollutant [5].

3.2. Effect of DAAB particle size on the fixed-bed adsorption column

Surface area and mono-dispersing of materials have strong affiliation with particle size of adsorbent as they are found to increase with reduction of the sizes which has influence in adsorption of

environmental pollutants. The effect of variation of particle size on the breakthrough curves shown in Fig. 3 revealed that the longest breakthrough increased with decrease in DAAB particle sizes.

This was reflected in the larger bed capacity of the column with smaller adsorbent particle sizes ($500\text{ }\mu\text{m}^{-1}\text{ mm}$, 58 mg/g) than the largest DAAB particle sizes of $2\text{--}3\text{ mm}$ with 38 mg/g capacity. The early breakthrough observed with larger particle sizes of DAAB was attributed to smaller mass transfer coefficient due to smaller specific surface area which also revealed the surface rated dependency of the sorption system [23]. Empirically, it can be said that adsorption performance of CO_2 on the DAAB was improved as the adsorbent particle sizes were reduced [24,25].

3.3. Effect of the activated alumina amine concentration on the breakthrough curves

The breakthrough curves of effect of diethanolamine concentration for modification of the activated alumina are presented in Fig. 4. The 0.8 M DAAB adsorbent had the longest breakthrough curve than 0.7 and 0.9 M DAAB adsorbents which translated to adsorption capacities of 55.94 , 38.26 and 45.16 mg/g respectively. Insufficient active sites on the 0.7 M DAAB adsorbent may be responsible for the low uptake observed while blockages of the pore width of the 0.9 M DAAB may have hindered physical trapping (physisorption) of the CO_2 molecules on the adsorbent surface [5].

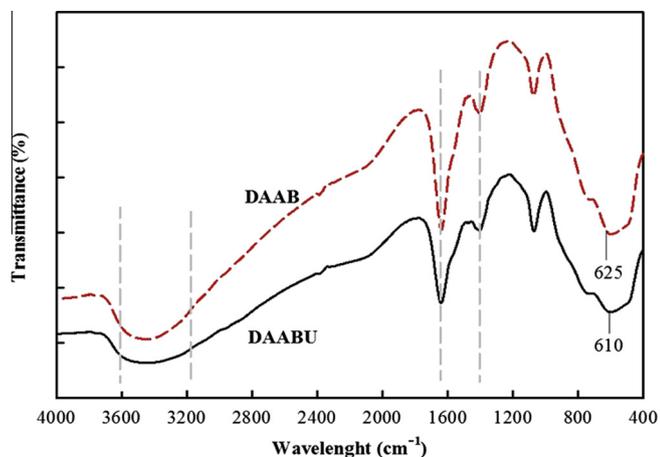


Fig. 2. The FTIR spectrums of activated alumina functionalized with diethanolamine before (DAAB) and after usage (DAABU).

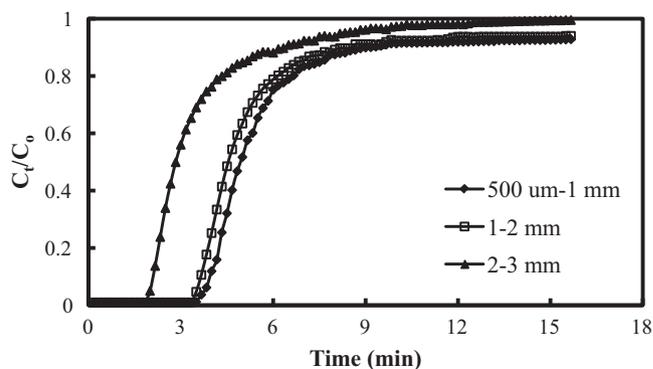


Fig. 3. The CO_2 adsorption breakthrough curve at different DAAB particles sizes, evaluated at temperature of $35\text{ }^\circ\text{C}$, feed flow rate of 90 mL/min , CO_2 concentration of 10% (balance of N_2), 0.8 M DAAB, bed height of 9.7 cm (3 g).

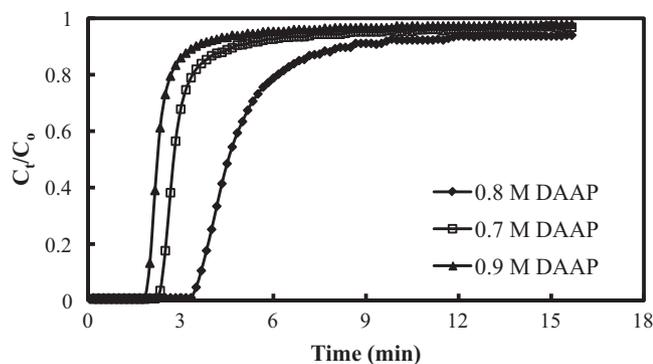


Fig. 4. The CO₂ adsorption breakthrough curve at different concentrations of diethanolamine used for functionalization, evaluated at temperature of 35 °C, feed flow rate of 90 mL/min, CO₂ concentration of 10% (balance of N₂), bed height of 9.7 cm (3 g), particle sizes of 1–2 mm.

3.4. Effect of variation of the feed flow rate on CO₂ adsorption by the DAAB adsorbent

The breakthrough curves profiles for variation of the feed gas mixture flow rate on the adsorption of CO₂ by the DAAB fixed adsorbent in the column are shown in Fig. 5. Adsorption of CO₂ molecules was rapid at the initial stages of the feed flow rate range (90–150 mL/min) studied due to availability of vacant active sites ready for adsorption activities. Lower flow rate (90 mL/min) of the inlet gas mixture was accompanied with low transport of the CO₂ molecules which gave ample diffusion coefficient that resulted to delayed breakthrough as can be seen in Fig. 5. An increase in the flow rate (120–150 mL/min) led to the reduction of the residence time of the adsorbate in the column leading to poor performance of the system or reduction on the adsorption efficiency [26,27]. This reflected on the adsorption capacities presented in Table 1 which were 55.94, 39.36 and 27.03 mg/g for the feed flow rates of 90, 120 and 150 mL/min, respectively. The experimental results showed that DAAB uptake of CO₂ was greatly affected by the feed flow rate which also implies that diffusion was not the only controlling mechanism but external mass transfer.

3.5. Effect of initial feed concentration on CO₂ adsorption by DAAB

The breakthrough curves of effect of initial feed concentration on CO₂ adsorption by DAAB are shown in Fig. 6. The number of molecules of carbon dioxide available per volume of the feed for adsorption by the DAAB was increased as the concentration of CO₂ was varied from 10 to 20%. This gave corresponding increase

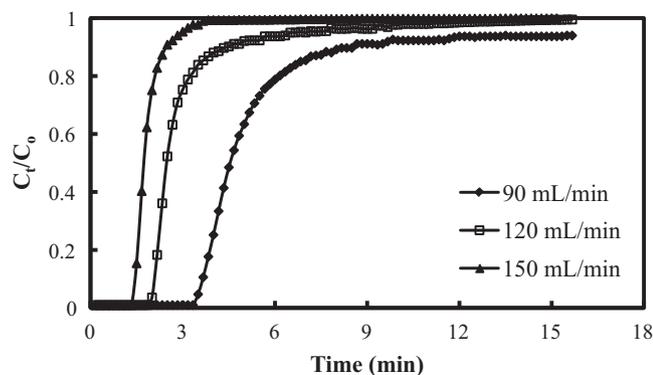


Fig. 5. The CO₂ adsorption breakthrough curve at different feed flow rates, evaluated at temperature of 35 °C, CO₂ concentration of 10% (balance of N₂), bed height of 9.7 cm (3 g), 0.8 M DAAB particle sizes of 1–2 mm.

Table 1

The DAAB CO₂ adsorption capacity and breakthrough time for parameters investigated.

Parameters	Values	Breakthrough time (s)	Adsorption capacity (mg/g)
CO ₂ % in the feed	10	930	55.94
	15	670	64.20
	20	600	70.20
Adsorption temperature (°C)	35	930	55.94
	45	610	31.56
	55	490	26.26
Feed flow rate (mL/min)	90	930	55.94
	120	486	39.36
	150	280	27.03
Amount of adsorbent in the adsorption column (g)	2	390	28.90
	3	930	55.94
	4	1020	67.27

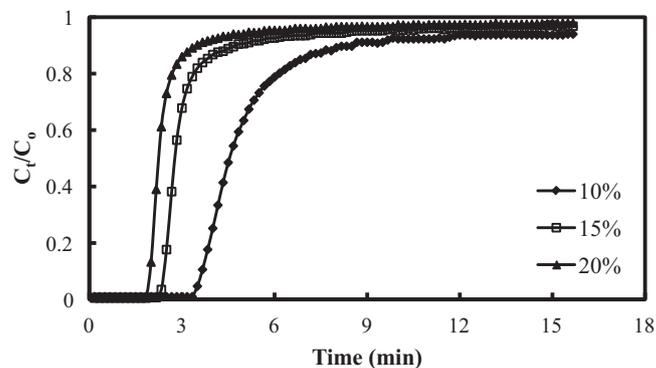


Fig. 6. The CO₂ adsorption breakthrough curve at different CO₂ concentration of the feed (balance of N₂), evaluated at temperature of 35 °C, feed flow rate of 90 mL/min, bed height of 9.7 cm (3 g), 0.8 M DAAB particle sizes of 1–2 mm.

of adsorption capacity of the adsorbent from 55.94 to 70.20 mg/g for the feed percentage increase of CO₂ from 10 to 20%, respectively (Table 1). The porosity of the DAAB enhanced physical adsorption while, the numerous amine groups on its surface (revealed by the FTIR spectrum) promoted chemical interaction with the CO₂ molecules which was found to be increasing with corresponding increase of the feed concentration. Increasing the feed concentration corresponded to increase in the concentration gradient or driving force and this led to shortening of the breakthrough point as depicted in Fig. 6. Consequently, decreasing the initial inlet (mixed CO₂ and N₂) concentration enhanced treatment of larger volume of the effluent as reflected by longer breakthrough curve due to reduced mass transfer or diffusion coefficient and slower saturation of the system [28].

3.6. Effect of adsorption column temperature on CO₂ capture

Effects of CO₂ capture temperature at various column temperatures (35, 45 and 55 °C) are presented in Fig. 7. The performance of an adsorbent with respect to the operating temperature gives information on its suitability in post or pre-combustion gas system. Unfavorable CO₂ capture was observed with increase in the adsorption column temperature such that the maximum capacities were 55.94, 31.56 and 26.26 mg/g for 35, 45 and 55 °C, respectively (Table 1). The CO₂ exothermic adsorption by DAAB was physisorptive which was attributed to the porous nature of the adsorbent as determined by the BET analysis. It was observed that lower temperature of adsorption promoted intense selective interactions

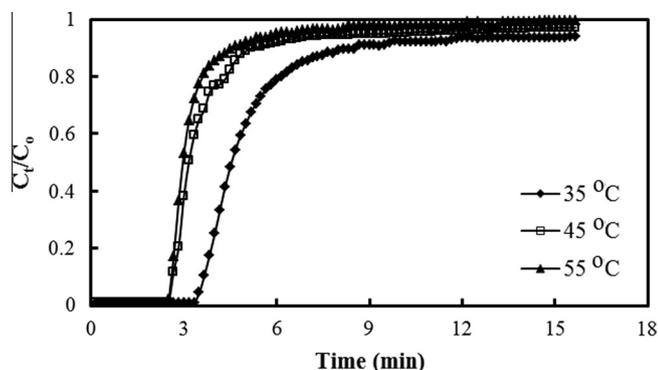


Fig. 7. The CO₂ adsorption breakthrough curve at different column temperatures, evaluated at feed flow rate of 90 mL/min, 10% CO₂ feed concentration (balance of N₂), bed height of 9.7 cm (3 g), 0.8 M DAAB particle sizes of 1–2 mm.

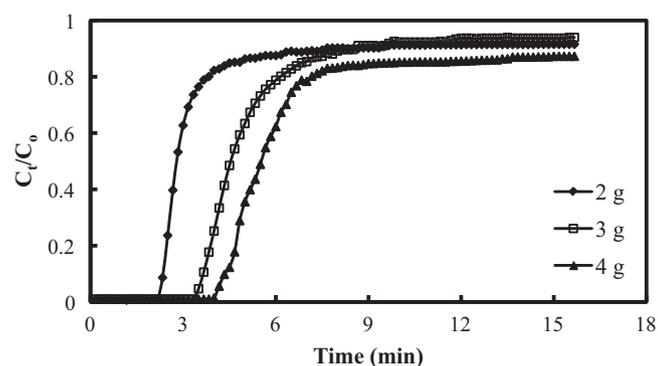


Fig. 8. The CO₂ adsorption breakthrough curve at different bed heights, evaluated at temperature of 35 °C, feed flow rate of 90 mL/min, 10% CO₂ concentration in the feed (balance of N₂), 0.8 M DAAB particle sizes of 1–2 mm.

between impregnated basic amine group on the activated alumina (DAAB) and the acidic CO₂ gas resulting to higher adsorption capacity; in a similar manner, carbon adsorbent modified with nitrogen compound showed higher adsorption of CO₂ gas at room temperature than at elevated temperatures [29].

3.7. Effect of DAAB bed height on CO₂ adsorption breakthrough curves

It is known that specific surface area and fixable binding sites for adsorbate is increased with increase in the adsorbent bed

height thereby leading to more volume of effluent gas treatment as a result of larger service area provided [30]. In this research, maximum adsorption capacities of 28.90, 55.94 and 67.27 mg/g were obtained for bed depth increments by addition of 2 (6.3 cm), 3 (9.7 cm) and 4 g (13 cm) DAAB, respectively. The breakthrough curves for effect of bed heights on the CO₂ adsorption are presented in Fig. 8. It is believed that shorter bed depths promotes axial dispersion due to insufficient contact period or interaction between the CO₂ gas molecules and the DAAB surfaces in the column adsorption experiments [31].

3.8. Comparison of adsorption capacity of DAAB for CO₂ uptake

The adsorption capacity of the functionalized activated alumina beads with 0.8 M ethylenediamine (DAAB) for CO₂ uptake (evaluated at temperature of 35 °C, feed flow rate of 90 mL/min, 10% CO₂ concentration in the feed (balance of N₂), 3 g of 0.8 M DAAB particle sizes of 1–2 mm) was compared with other adsorbents in the literature. An appreciable sorption capacity exhibited by the DAAB was attributed to the presence of some amine groups emanating from the modification carried out. Vivid comparison of the CO₂ sorption capacity of DAAB adsorption can be seen in Table 2.

3.9. Reusability of DAAB for CO₂ adsorption

Adsorbent reusability is an excellent quality for economic viability of adsorption processes as it aids in efficient treatment of effluents [2]. The DAAB adsorbent was subjected to thirteen multi-cycles adsorption at a synthetic flue gas (CO₂ and N₂) flow rate of 90 mL/min, DAAB mass of 3 g, column temperature of 35 °C, CO₂ feed stream concentration of 10% and DAAB particle size of 1–2 mm. The DAAB reusability adsorption capacities for the thirteen multi-cycles are shown in Fig. 9.

Observation showed that stability in adsorption capacity of the DAAB was approximately maintained except for the sudden drop after the first cycle. The sorption capacity for the first, second and the thirteenth runs were 55.94, 52.48 and 51.88 mg/g, respectively; there was about 6.4% drop in the DAAB capacity during the thirteenth run. Some residual chemisorbed molecules of the CO₂ that could not be removed at 110 °C may have contributed to the sudden decline in the DAAB capacity [37]. This pattern of adsorption exhibited by DAAB was similarly observed with 3-aminopropyltriethoxysilane/silica fume sorbent employed for multiple CO₂ adsorption/desorption cycling tests [38].

Table 2

Comparison of adsorption capacity of adsorbents for CO₂ adsorption.

Adsorbent	CO ₂ % in the feed	Adsorption temperature (°C)	Feed flow rate (mL/min)	Adsorption capacity (mmol CO ₂ /g)	Refs.
DAAB	10	35	90	1.27	This study
TEPA ^a -MCM-41	10	35	–	2.7	[8]
EDA ^b -MCM-41	10	35	–	0.7	[8]
Amine-impregnated titanium oxide	10	75	20	2.24	[9]
DWSNT ^c -NH-(CH ₂) ₂ -NH-(CH ₂) ₂ -NH ₂ ^d	–	25	–	2.23	[32]
Amine-based sorbent	1	30	300	1.92	[33]
Carbon vulcan XC72R modified with paraphenylenediamine	100	40	100	0.24	[34]
3-Aminopropyltrimethoxysilane-grafted mesoporous SAPO-34	–	25	–	1.77	[35]
TEPA ^e -TiNT ^f -69	15	60	40	4.37	[36]

^a TEPA-MCM-41 is tetraethylenepentamine.

^b EDA is ethylenediamine.

^c DWSNT is double-walled silica nanotube.

^d NH-(CH₂)₂-NH-(CH₂)₂-NH₂ is 3-[2-(2-aminoethylamino) ethylamino] propyl-trimethoxysilane.

^e TiNT is TiO₂ nanotubes.

^f TEPA is tetraethylenepentamine.

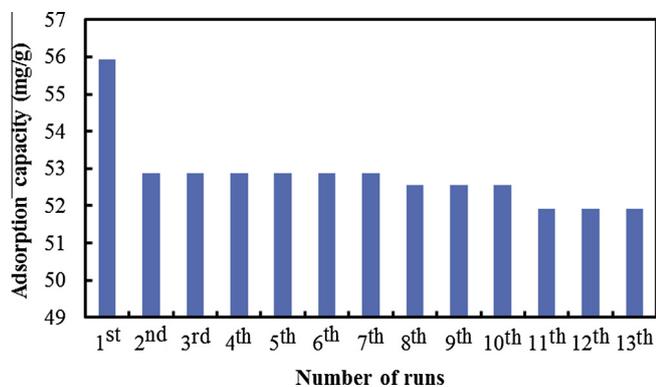


Fig. 9. The 0.8 M DAAB multi-cycle CO₂ adsorption test evaluated at temperature of 35 °C, feed flow rate of 90 mL/min, 10% CO₂ concentration in the feed (balance of N₂), 3 g of DAAB particle sizes of 1–2 mm.

4. Conclusion

Mesoporous activated alumina was functionalized with diethanolamine and used for selective adsorption of CO₂ from its mixture with nitrogen. The study revealed that the optimum DAAB CO₂ adsorption was at 90 mL/min flow rate, column temperature of 35 °C and CO₂ feed stock concentration of 10%. Modification of the 1–2 mm particle size alumina with 0.8 M diethanolamine gave the best CO₂ adsorption performance. Characterization of the DAAB revealed shrinking of the pore size in the N₂-adsorption test and successful functionalization by the presence of N₂ group in the energy dispersive X-ray microanalysis spectrum. Multi-cycle DAAB CO₂ adsorption experiment revealed that the adsorbent can be reused a number of times before discarding. The DAAB is a promising adsorbent for alleviation of CO₂ pollutant.

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