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

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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 (CO_2/N_2).
- 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 (CO_2) 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 CO_2 in the feed stream revealed that 90 mL/min, 35 °C, 3 g and 10% of CO_2, respectively were the optimum operating conditions for the highest adsorption capacity of 55.94 mg/g. The DAAB multi-cycle CO_2 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 CO_2 pollutant molecules.

1. Introduction

An easy to use, regenerate, multi-cycle and high adsorption capacity adsorbent is the yenning 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 CO_2 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 (NH_3, amines etc.), decomposition of surface acidic functional groups through calcinations [7]. Amine modification of adsorbents for capturing CO_2 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 CO_2 within the mesopores [10,11]. The modified (amine) adsorbent ability to promote CO_2 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 CO_2. 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 CO_2 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 CO_2 capturing but it requires energy for regeneration and also

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causes corrosion [5,10]. Despite these limitations, enhancement of effective adsorption and lowering of carbamate (product of CO_2 adsorption on amine reaction ($CO_2 + 2R–NH_2 = R–NHCOO– + R–NH_3^+$)) 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 CO_2 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 CO_2 adsorption reports is limited in literature [13,15,16].

In this study, mesoporous activated alumina was synthesized with diethanolamine through impregnation for adsorption of CO_2 in a fixed bed column. The relationship between the resulting breakthrough curves of the CO_2 adsorption on the DAAB adsorbent and the adsorption parameters (temperature, concentration, flow rate, bed height, CO_2 %) 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 CO_2 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% CO_2) and nitrogen (balance of CO_2% 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 CO_2 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 CO_2 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 CO_2 adsorption in the fixed-bed column were studied. The column adsorption temperature range selected covers a typical post flue gas desulphurization range of 45–55 °C [17].

2.4. Regeneration of adsorbent

The CO_2 adsorbed on 3 g (1–2 mm size) DAAB at 35 °C of 10% CO_2 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 CO_2 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 CO_2 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 m^2/g for DAAB as compared with 5.7 nm and 207 m^2/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 CO_2 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