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Fixed-bed column adsorption of carbon dioxide by sodium hydroxide modified activated alumina

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HIGHLIGHTS

- Activated alumina was modified with 30% NaOH and calcined at 500 °C for 4 h (3MAA).
- Physical and chemical characterization of the adsorbents were carried out.
- Carbon dioxide was adsorbed from CO_2/N_2 mixture in a continuous adsorption system.
- Regeneration of the 3MAA were successfully tested for three cycles.

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ABSTRACT

Activated alumina was successfully modified with sodium hydroxide (NaOH) and used for capturing of CO_2 in fixed-bed column adsorption system. Calcinations temperature (200–500 °C), time (2–4 h) and concentration of NaOH (10–40%) suitable for the modification were studied. Surface area and porosity, morphology/elemental composition, crystal structure and functional groups of the plain activated alumina (PAA) and optimally modified adsorbent with 30% NaOH calcined at 500 °C for 4 h (3MAA) were characterized using nitrogen adsorption–desorption, scanning electron microscopy/energy dispersive X-ray, X-ray diffraction and Fourier transform infrared spectroscopy techniques (4000–500 cm^{-1}). The effect of CO_2 % in the feed, adsorption temperature, 3MAA particle sizes, feed flow rate and amount of 3MAA in the column were investigated in the adsorption experiments. Adsorption capacity of 3MAA and PAA were 51.92 and 19.61 mg/g even with their surface areas of 203 and 207 m^2/g, respectively. The enhanced adsorption on 3MAA was due to its average pore width and total pore volume which were larger than those of PAA. Physisorption activities that characterized the nature of the 3MAA adsorption, enhanced easier desorption of CO_2 conveniently for three cycles. The results of this study have revealed that sodium hydroxide modified activated alumina can be applied for CO_2 pollution control in the environment.

1. Introduction

There is a necessity for more proactive action in tackling air pollution since it is a more global challenge than other forms which can be localized. Air occupies the entire universe and has its pollutants along with it. Carbon dioxide (CO_2) among other air pollutants is a major culprit to the greenhouse gases that is fueling global warming. It can be sourced from aerospace industry, hydrogen gas production, hydrocarbons purification, treatment of natural gas and a major source like fossil fuel which accounts for 25 billion tons that is released to the atmosphere annually [1,2]. And presently, the world energy source is largely dependent on fossil fuel with cleaner greener renewable alternative energy sources still in developmental stages [3]. The need to contain CO_2 emission aside guiding against the greenhouse effect, is to aid in accomplishing absolute air and natural gas purification amongst others.

Measures such as zero CO_2 emission technologies, point source capture and sequestration are attempts made to check CO_2 pollution effect [4]. New plants with zero CO_2 emission have also attempted using membrane science, cryogenic distillation, solvent absorption, fixation using algae and adsorption methods with a view to salvaging the pollution challenge [4,5]. The high efficiency, affordable energy and application of less resources using adsorption for CO_2 capture has made the process outstanding from others [2,6].

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Various adsorbents such as hydrotalcite and inorganic-porous materials, activated carbons, basic oxide and amine-based have been employed in catalysis and adsorption of CO_2 pollutant from the environment [7–10]. But some of these adsorbents like the amine based require high energy and possess degradation threat through oxidation that results in corrosion [11]. Some commercial adsorbents have low selectivity and low capability of CO_2 adsorption [3].

In the quest for more efficient and effective CO_2 capturing adsorbents, few studies have been conducted on the use of transition, activated and modified alumina. But it has been proven that on the surface of alumina lies chemical and physical active sites that has affinity for CO_2 molecules [6,12,13]. This may be attributed to alumina amphoteric nature that is the ability to withstand or dissolve in both acid and base solution [14].

In this work a cost effective, low energy intensity, environmental friendly and high capacity adsorbent from activated alumina for CO_2 adsorption was developed. The carbon dioxide was adsorbed from a mixture of CO_2/N_2 since flue gas emissions are often associated with considerable amount of nitrogen gas [15]. The percentage of sodium hydroxide (NaOH) used for modification, calcinations temperature and time were studied. The fixed-bed adsorption experiment involved study of the effect of some process parameters such as effect of flow rate, bed height and influent CO_2 concentration, adsorbent particle size and adsorption temperature on the breakthrough curves.

2. Materials and methods

2.1. Materials

Activated alumina of 1–2 mm particle sizes was supplied by OMI (M) Sdn. Bhd., Malaysia. Sodium hydroxide was purchased from Mercks Chemical company, while purified carbon dioxide (99.9%) and nitrogen (99.9%) gases were supplied by Wellgas Sdn. Bhd., all in Malaysia.

2.2. Preparation of CO_2 adsorbent

The activated alumina beads were slightly washed with distilled water and dried in an oven at 110 °C for 6 h. The dried beads were packaged in air tight container and used as unmodified or plain activated alumina (PAA) adsorbent.

Ten grams of unmodified activated alumina was treated with 30 mL of different concentration (10–40%) of NaOH and allowed to dwell for 2 h. The treated unmodified activated alumina beads according to the percentage of NaOH used were designated as follows: 1MAA, 2MAA, 3MAA and 4MAA for 10%, 20%, 30% and 40%, respectively. Afterwards, the NaOH solution was decanted from the beads and then dried in an oven at 110 °C for 6 h before calcinations at various temperatures (200–500 °C) and time (2–4 h) [16]. Excess sodium on the surface of the adsorbent was evacuated by washing with distilled water while monitoring the pH after which it was dried and packaged for further use [17,18].

2.3. Fixed-bed column adsorption

The adsorbent was measured into the adsorption column and dried by heating to 110 °C under an inert atmosphere and allowed to dwell for 1 h before cooling to the desired adsorption temperature. A mixture of high purity nitrogen gases was passed through an adsorption column of length 42 cm and a diameter of 1.1 cm in an upward flow. The inflow of each gas from the cylinders were controlled by a calibrated mass flow controller AALBORG (model AFC26 NY, USA). The amount of CO_2 adsorbed after every 10 s was determined by an online carbon dioxide analyzer model 906 (Quentek instrument, USA).

The effect of adsorption parameters such as percentage of CO_2 in the feed stream, flow rate, adsorption temperature and bed depth were studied. The percentage of CO_2 in the feed stream varied from 12%, 15% and 18%; the influent flow rate of 90, 120 and 150 mL/min; 35(±), 45(±) and 55(±) °C were the temperatures varied for the adsorption process; and the amount of adsorbent (PAA and MAA) were 2, 4 and 6 g.

The adsorption experimental breakthrough curves were generated by the Carbon dioxide analyzer and relayed in the desktop computer attached to it.

2.4. Regeneration of adsorbent

At the end of an adsorption process, the adsorption column with the adsorbent fixed on it was heated up to 110 °C for 1 h under nitrogen gas flow to desorb molecules of CO_2 adsorbed on the 3MAA surface. The stability of desorption was ascertained by passing the column exit gas through the CO_2 analyzer until the residual CO_2 concentration was steady. The column was purged using a vacuum pump for 30 min to remove the trapped gas in the adsorbent. Then another cycle of CO_2 adsorption was carried out and similar procedure was repeated for three cycles of adsorption–desorption. During the reusability test, the column conditions such as adsorption temperature (35 °C), percentage of CO_2 (15%) in the feed (85% balance of N_2), total feed flow rate (90 mL/min), amount of adsorbent used (4 g) and adsorbent size (1–2 mm) were kept constants.

2.5. Characterization of adsorbents

The PAA and 3MAA surface area and porosity were determined by Brunauer–Emmett–Teller (BET), morphology and elemental composition using scanning electron microscopy and Energy-dispersive X-ray spectroscopy technique. The crystal structure and functional groups of the adsorbents were analyzed using X-ray diffraction and Fourier transform infrared spectroscopy techniques, respectively.

An autosorb Brunauer–Emmett–Teller Micrometric ASAP 2020 operating with the static volumetric technique was used to determine the surface area and porosity of the adsorbent. Samples were degassed at 300 °C for 2 h measurement of equilibrium pressure of a known volume of liquid nitrogen for the generation of adsorption–desorption isotherms. Barrett–Joyner–Halenda and t-plot method were used to evaluate the average pore size distribution cum total pore volume, respectively while the BET equation was used to calculate the surface area.

An integrated scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) microanalysis (Oxford INCA 400, Germany) was used to determine the physical morphology and chemical composition of plain and modified activated alumina adsorbent. The bead samples were attached to an aluminum stub with a carbon tape before placement in the analysis chamber for scanning.

A Siemens XRD D5000 diffractometer that is equipped with Cu Kα radiation at a beam voltage of 40 kV with a scanning rate of 2° per minute recording between 5° and 90°, was used to determine the crystal structure of unmodified and modified activated alumina adsorbents. The small glancing angle was fixed at 2θ.

Fourier transform infrared spectroscopy (FTIR) analysis was applied to determine the surface functional groups on the adsorbents. After 100 times of scans, spectra between 4000–400 cm^{-1} were taken using potassium bromide (KBr) as the mulling agent. Both the KBr and samples were dried overnight in an oven at 110 °C before mixing together in a 5% adsorbent and balance KBr. A 7 mm diameter of 1 mm thickness was formed with the aid of hydraulic press prior to analysis.