

Diethanolamine impregnated palm shell activated carbon for CO₂ adsorption at elevated temperatures



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ABSTRACT

The CO₂ adsorption characteristics of palm shell activated carbon (AC) impregnated with monoethanolamine (MEA) and with diethanolamine (DEA) were compared. The impregnation of the AC with 3% MEA and 3% DEA yielded loadings of 2.46 mol MEA/kg AC and 1.33 mol DEA/kg AC, respectively. The impregnation with MEA and DEA caused reductions of micropore surface areas by 52% and 11%, respectively. The saturation adsorption capacities of the AC-DEA were found to be above those of the AC-MEA at 40–70 °C. A maximum CO₂ adsorption capacity of 5.3 mol/kg was obtained for the AC-DEA at 400 kPa and 70 °C. Under atmospheric pressure, the breakthrough capacities of the AC-MEA samples were lower than those of the AC-DEA samples at all temperatures investigated. The saturation capacities of the AC-MEA were also lower than for the AC-DEA by approximately the same percentages as for the breakthrough capacities. At the regeneration temperature of 160 °C, the regeneration times for the AC-MEA were found to be at least 20 min longer than the times for the AC-DEA. This difference was possibly due to higher intraparticle mass transfer resistance in the AC-MEA than in the AC-DEA. Based on both adsorption and desorption characteristics, DEA was suggested to be a more suitable impregnating agent for palm shell activated carbon.

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1. Introduction

Carbon dioxide (CO₂) is a greenhouse gas that is released from burning fossil fuels. It has been realized that CO₂ plays a crucial role in climate change [1]. CO₂ is also a major component in biogas, which typically consists of methane (CH₄) 55–80%, CO₂ 20–45%, trace amounts of hydrogen sulfide (H₂S) 1000–5000 ppm, moisture and other impurities [2]. CO₂ separation from biogas, followed by CO₂ capture and storage, not only reduces risks of machinery and instruments deterioration, but also helps decrease the CO₂ concentration in the atmosphere.

Adsorption is a method that has received considerable research interests in the last decade. A variety of potential adsorbents for CO₂ capture from mixed gases have been reported, including activated alumina [3,4], activated carbon [5–10], mesoporous

carbons [11,12], carbon fiber [13,14], carbon nanotubes [15–17], mobil catalytic material No.41 (MCM-41) [18], TiO₂ nanotubes [19], and zeolite [20–25]. Among these, activated carbon (AC) offers an attractive and relatively inexpensive adsorbent for CO₂ separation and capture.

An impregnation process has been successfully used as a method to introduce amine-based molecules onto the surface of AC. Amine-impregnation has been claimed to be a convenient method for increasing CO₂ adsorption, especially at temperatures between 60 °C and 70 °C [22,26–28]. Amine-impregnation was found to help increase the selectivity of AC towards polar molecules such as CO₂ because amine groups provide specific adsorption sites of a stronger nature than van der Waals forces [22]. Two amine-based molecules commonly used in industry are monoethanolamine (MEA) and diethanolamine (DEA). Market prices of MEA and DEA are approximately the same. However, the degradation products of DEA are known to be much less corrosive than those of MEA [29,30]. In addition, the boiling point of DEA (271 °C) is much higher than that of MEA (170 °C). This higher boiling point suggests that DEA-impregnated AC may be used

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without material degradation at higher operating temperatures than MEA-impregnated AC.

In the present study, surface characteristics, CO₂ adsorption capacities and regeneration characteristics of MEA- and DEA-impregnated AC were compared. Static and dynamic CO₂ adsorption capacities were investigated at temperatures between 40 °C and 70 °C. The temperature that may cause material degradation and prohibit reusability of the adsorbents was identified for both MEA- and DEA-impregnated AC.

2. Materials and methods

2.1. Materials

All chemicals used were of analytical grade. Commercially available AC (C. Gigantic Carbon Co., Ltd., Thailand) produced from steam activation of palm shell was used as the adsorbent. MEA and DEA of higher than 99% purity were obtained from Carlo Erba (Italy). Properties of MEA and DEA are listed in Table 1. Methanol (Carlo Erba) was used as the solvent in MEA and DEA solutions. The CH₄ and CO₂ used to prepare the CH₄/CO₂ gas mixture for test samples were of high purity grade (HP 99.995%). The helium (He) used for volume measurements and the nitrogen (N₂) used for pretreatment of the adsorbent and regeneration of the exhausted adsorbent were of ultra high purity grade (UHP 99.999%). Distilled water was used throughout the study.

2.2. Wet impregnation

The procedure of Bezerra et al. [22] was followed. The AC sample was washed with distilled water to remove fines and dirt and then dried at 110 °C for 24 h. One gram of AC was immersed in 5 mL of 3% w/v MEA in methanol and in 5 mL of 3% w/v DEA in methanol. The samples were agitated at room temperature (30–34 °C) for a period of 15 min and then placed in a water bath at 70 °C to allow slow evaporation of the solvent. Finally, the AC impregnated with MEA (AC-MEA) and the AC impregnated with DEA (AC-DEA) were dried overnight in a vacuum oven (Memmert, VO 500, Germany).

The quantity of chemical agent deposited on to a sample of adsorbent during the impregnation was calculated from the difference between the initial dry weight and the final dry weight of the same sample after impregnation. The mass loading ratio of impregnating agent was calculated as the quantity of the agent normalized by the original adsorbent weight.

2.3. Surface characterization

BET surface area, pore volume and pore size of the unimpregnated and impregnated adsorbent samples were determined by a N₂ adsorption method at –196 °C (Quantachrome, Autosorb-1C, USA). The BET surface area was evaluated based on the

Brunauer, Emmett and Teller (BET) method. Pore volume and pore size from the desorption isotherm were calculated by the Barrett–Joyner–Halenda (BJH) method. External and micropore surface areas were calculated by the *t*-plot method. The IR spectra of the unimpregnated and impregnated adsorbent samples were measured by a Fourier Transform Infrared (FT-IR) spectrometer (Bruker, Equinox 55, Germany) using the potassium bromide (KBr) technique. The sample peaks in the wavelength range of 4000–400 cm^{–1} were analyzed. Thermal degradation as a function of temperature of the unimpregnated AC and the impregnated AC was determined by Thermogravimetric analysis (TGA) technique using a Thermogravimetric analyzer (PerkinElmer, TGA 7, USA). Twenty mg of each sample were heated from 25 °C to 1000 °C at the rate of 10 °C/min under N₂ atmosphere. The weight loss and the rate of weight loss were recorded. Elemental analysis of the samples was performed by a CHNS-O analyzer (Thermo Quest, Flash EA 1112 series, Italy).

2.4. Static adsorption

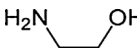
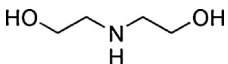
The experimental apparatus used the static volumetric method previously reported in Khunpolgrang et al. [31]. The main components of the apparatus were an adsorption cell and a loading cell. Approximately 1 g of each adsorbent was placed in the adsorption cell. The adsorbate (e.g. CO₂) was introduced into the loading cell, and after the pressure and temperature in the loading cell stabilized, the adsorption step was carried out by allowing the gas to expand to the adsorption cell. Pressure measurements were made in the range of 20–500 kPa and temperature measurements in the range of 40–70 °C. The adsorption equilibrium state was considered to have been achieved when the temperature and the pressure of the system were constant.

2.5. Dynamic adsorption

Dynamic adsorption experiments were performed in a single-column with a height of 0.84 m and a diameter of 0.02 m. The adsorption column was filled with 160 g of the fresh adsorbent. A grid and mesh was fitted at the top and the bottom to support the packed bed of the adsorbent and to retain fine particles. Before the dynamic adsorption test, the adsorbent was treated with N₂ at an upward flow rate of 100 mL STP/min under a pressure of 100 kPa at 110 °C for 90 min. The system was then evacuated to a pressure below 30 kPa. For the following dynamic adsorption study, a gas mixture consisting of 40% CO₂ with balance CH₄ was fed in at the bottom of column at a flowrate of 2.0 L STP/min. To set the conditions for isothermal processing, the adsorption column was wired with heating tape and covered with a heat insulator. At the top of the column, the CO₂ concentration was periodically analyzed by a gas chromatograph coupled with a thermal conductivity detector (Shimadzu, GC-2014, Japan). The breakthrough capacity of an adsorbent for CO₂ (BC_{CO₂}) is defined as the amount of CO₂ trapped in the adsorbent before CO₂ can be detected in the gaseous effluent stream. The experiments to determine the breakthrough point were performed under atmospheric pressure at four different temperatures: 40 °C, 50 °C, 60 °C and 70 °C. The saturation capacity of an adsorbent for CO₂ (SC_{CO₂}) is defined as the amount of CO₂ trapped in the adsorbent before CO₂ concentration in the gaseous effluent stream reaches the same level as the inlet concentration. BC_{CO₂} and SC_{CO₂} were calculated from Eqs. (1) and (2), respectively [32].

$$BC_{CO_2} = \frac{Qx_{CO_2}}{22.4m_i} \left(t_b - \int_{t_0}^{t_b} \frac{C_t}{C_0} dt \right) \quad \text{mol CO}_2/\text{kg} \quad (1)$$

Table 1
Physical properties and chemical structures of MEA and DEA.

Properties	MEA	DEA
Chemical structure		
Molecular weight (g/mol)	61.08	105.14
Boiling point (°C)	170	271
Melting point (°C)	10.3	28.0
Density (g/cm ³)	1.012	1.097
Vapor pressure (Pa) (20 °C)	64	<1

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