



Synthesis of porous carbon monolith adsorbents for carbon dioxide capture: Breakthrough adsorption study

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ABSTRACT

Carbon monoliths with bimodal porosity were obtained through nanocasting technique from silica monoliths (hard template) and furfuryl alcohol (precursor). These carbon adsorbents were evaluated as sorbents for CO₂ capture by using a fixed-bed adsorption set up under dynamic conditions. Carbonization at different temperatures (550 to 950 °C) was carried out that resulted in the generation of different carbon adsorbents containing oxygen functional groups. The textural characterization results reveal the effect of nanocasting technique, which is confirmed from the generation of mesopores (0.41), micropores (0.85 cm³ g⁻¹) and high surface area (1225.1 m² g⁻¹) of adsorbent synthesized at 950 °C, as shows highest CO₂ uptake of 1.0 mmol g⁻¹ at 30 °C and 12.5% CO₂ concentration. The increase in the adsorption capacity with increasing CO₂ concentration and decrease with the increasing adsorption temperature confirms the physisorption process. Five adsorption–desorption cycles show established materials with excellent regeneration stability as an adsorbent. Furthermore, three kinetic models along with three isotherms were used in the present study to analyze the adsorption data and found that fractional order kinetic model and Temkin isotherm fitted best. Thermodynamic studies suggested the exothermic, spontaneous as well as the feasible nature of the adsorption process.

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1. Introduction

In the Earth's atmosphere, major greenhouse gases, including methane (CH₄), nitrous oxide (N₂O), carbon dioxide (CO₂), and ozone (O₃), is considered responsible for rapid climate change and among these gases CO₂ is the second largest contributor to the global warming after water because of its emission has been identified as a main contributor to the atmosphere. The anthropogenic CO₂ emissions are almost entirely caused by combustion of fossil fuels like coal and natural gas to produce energy [1, 2]. The CO₂ concentration increased from 280 ppm to 406.75 ppm at present year (2018) [3] which is expected to increase up to a level of 570 ppm by 2100 [4] which will rise the global surface temperature and create problem such as climate change, increase in the acidity of oceans and serious health issues for the living-beings [5, 6]. Currently, carbon capture and storage (CCS) technology are the important technology to reduce the concentration of CO₂ and play a significant role to obtain the required reduction in greenhouse gas (GHG) emissions [7]. CCS includes three basic types: post-

combustion, pre-combustion and oxy-fuel combustion capture. The most widely adopted technology is the post-combustion for CO₂ capture from emission source due to its flexibility and ease of retrofit to existing combustion technologies [8]. It includes chemical absorption, cryogenic separation, adsorption, membrane separation and biological fixation [9, 10]. Among the various methods, the chemical solvent absorption for CO₂ capture is efficient but it requires a large amount of energy for regeneration due to the large emission of flue gases and low CO₂ concentration. Also, it causes equipment corrosion and need for a large absorber volume [11].

CO₂ capture by adsorption method is considered one of the potential in terms of cost-effective options because of the cost advantage, low energy consumption and ease of applicability over a wide range of temperature and pressure. However, the choice of the adsorbents with high CO₂ selectivity and adsorption capacity, high stability, and easy regenerability make it successful [10, 12]. The CO₂ adsorption on solid adsorbents, including porous carbons [13], amine-modified silicas [14], zeolites [15], and metal-organic framework compounds [16] have received considerable research interest recently. Carbon-based materials are considered to be one of the outstanding materials for CO₂ adsorption due to their large surface area [17], wide availability [18], low cost [19], adjustable porosity [20] and low energy for regeneration [17]. On the other hand,

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carbon based adsorbents are versatile adsorbing materials and possess a wide range of morphologies both on the macroscopic and microscopic level [21]. Macroscopically, a monolith shows the wide flexibility of operation in contrast to its powder counterparts and microscopically, the structure of monolith is represented by its 3D bicontinuous hierarchical porosity, which exhibits significant advantages such as fast heat and mass transfer, low pressure drop, easy to deal, and high contacting efficiency [22–24]. It is reported that, the micropores as well as macropores are highly beneficial for adsorption of CO₂. Micropores are most suitable for trapping of CO₂ gas whereas macropores provided the low resistant pathways for diffusion of CO₂ molecules [25]. Goel et al. [26] developed mesoporous carbon adsorbent from resin (melamine-formaldehyde) and mesoporous silica by nanocasting method. The CO₂ adsorption performance was evaluated thermogravimetrically at different temperatures (30–100 °C) and CO₂ concentrations (10–100%) and obtained that adsorbent prepared at 700 °C showed highest CO₂ adsorption capacity of 0.79 mmol g⁻¹ under 100% CO₂ flow at 30 °C. Hao et al. [25] synthesized nitrogen-doped carbon monoliths by carbonization of formaldehyde and resorcinol using L-lysine (catalyst). The CO₂ adsorption capacity of these monoliths, determined volumetrically, was found to be 0.62 mmol g⁻¹ at 120 °C under static conditions at 1 bar pressure. Hosseini et al. [27] synthesized carbon monoliths by using furfuryl alcohol and polyethylene glycol and obtained CO₂ uptake of 0.52 mmol g⁻¹ for 15% CO₂ concentration at 30 °C. Moreover, monoliths modified with NH₃ and KOH and they achieved CO₂ uptake of 0.58 mmol g⁻¹ and 0.66 mmol g⁻¹, respectively. The current literature study shows that only very few references are available for CO₂ capture performance on the carbon monolith adsorbents under dynamic conditions. Also, the performance evaluations are mainly carried out under static conditions and the mostly synthesis was done by direct carbonization process which is not possible to control the specific pore structure of the adsorbent. However, using nanocasting technique, the textural and surface properties of the adsorbent can be easily tuned [13] which plays an important role in CO₂ adsorption. In addition, most of the reported CO₂ capture studies have been limited to equilibrium uptake measurements as compared to more industrially relevant dynamic capacity and regeneration. Further, the performance evaluation which is carried out under static conditions will not give a true picture from carbon capture and storage (CCS) point of view [28]. Hence, it is need to develop an efficient synthesis for porous monolithic carbons which exhibit good CO₂ adsorption and high selectivity towards CO₂ and also, overcome the problems caused by powder carbons.

Herein, carbon monolith adsorbents with bimodal porosity (micro-/meso-pores) have been synthesized by using nanocasting technique for CO₂ adsorption and the effect of adsorption temperature (30–100 °C) and CO₂ concentration (5–12.5%) on the adsorbent under dynamic conditions were investigated. Also, the kinetics, adsorption isotherm, regenerability, selectivity and thermodynamic studies have been carried out.

2. Experimental

2.1. Materials

Tetraethylorthosilicate (TEOS) was supplied from Alfa Aesar. Octadecyltrimethylammonium bromide (CTAB) and polyethylene glycol (PEG, MW 35,000 g mol⁻¹), were purchased from Sigma-Aldrich. Trimethyl benzene (TMB), furfuryl alcohol (FA, 98%), oxalic acid and hydrofluoric acid (HF, 40%) were purchased from Loba Chemie, India. Ammonia (28–30%) and nitric acid (69%) were purchased from Merck. Helium gas (99.995%), carbon dioxide gas (99.999%) and nitrogen gas (99.995%) used in this study were supplied by M/s. Sigma Gases and Services, India.

2.2. Preparation of carbon monoliths via nanocasting

The preparation of the silica monolith (SM) was done by sol-gel method [29]. Initially, nitric acid was added in the solution of PEG and water. TEOS was added after the dissolution and stirred the solution for 10–15 min at room temperature until it become translucent. Then, CTAB surfactant was dissolved into the solution with continuous stirring. The molar ratio of H₂O: HNO₃: TEOS: PEG: CTAB was taken 16.5: 0.53: 2.2: 9.5 × 10⁻⁴: 0.2 for the synthesis of the SM [30]. The achieved sol was shifted to microplates and kept for 72 h at 40 °C for sol to gel formation. Then, the SMs were soaked in NH₄OH solution (1 M) at 90 °C for 9 h followed by acidification with 0.1 M nitric acid solution. Later, monoliths was washed with de-ionized water by 5–7 times and kept for drying at 40 °C for 4 days. Finally, the SMs were calcined at 550 °C for 5 h with the heating rate of 1 °C min⁻¹.

The carbon monoliths were synthesized [31] as follows: Hard template silica monoliths were impregnated by precursor solution (FA, oxalic acid, and TMB where FA: oxalic acid = 250, by molar ratio) after degassing in a vacuum. On the completion of impregnation (three times), the resulted monoliths found to be translucent. Then polymerization carried out at 50 °C and 90 °C for 24 h at each temperature. Afterwards, monoliths were carbonized under an N₂ atmosphere (60 ml min⁻¹) at different temperatures from 550 to 950 °C for 4 h with the heating rate of 2 °C min⁻¹ after isothermal at 150 °C for 3 h. Finally, silica part was removed by etching with 10% (by volume) HF solution for 24 h. Schematic diagram of the synthesis process for carbon monoliths with the parent silica is shown in Fig. 1. The resulting carbon monoliths were washed at least four times with water and then dried in an oven at 100 °C for 10 h and denoted as CMT, where *T* stands for carbonization temperature (550–950 °C).

2.3. Characterization of the adsorbents

X-ray diffraction analysis of the adsorbents was performed by PANALYTICAL X'Pert PRO diffractometer with Cu K_{α1} radiation (λ = 1.5406 Å) operated at 45 kV over a 2θ range of 10°–80°. The SEM (scanning electron microscope) images of the samples were collected by JEOL-JSM – 6510 SEM. The accelerating voltage was 20.0 kV. The high-resolution transmission electron microscopy (HRTEM) images were obtained on FEI TECNAI G2 F20, Netherlands operated at 200 kV. The Elemental analysis of the adsorbents was analyzed by Thermo Scientific Flash 2000 organic elemental analyzer. Fourier transform infrared spectroscopy (FTIR) was done by Perkin Elmer Spectrum 100 FTIR spectrophotometer over the wavenumber range of 4000–500 cm⁻¹. The BET surface area and pore sizes were analyzed through BET surface area analyzer of Bel, Japan, Inc (Microtec BELSORP MINI-II). The total pore volume was calculated at a relative pressure range (P/P₀ = 0.99) with the amount of nitrogen adsorbed and the pore size distribution (PSD) curves were collected from Barrett–Joyner–Halenda (BJH) model. The micropore size distribution analysis attained by MP plot method. Surface characterization of the monoliths was done by X-ray photoelectron microscopy (XPS, Omicron ESCA+) with monochromated aluminium source (Al ka radiation at 15 V, hv = 1486.7 eV).

2.4. CO₂ adsorption experiments

The dynamic CO₂ adsorption–desorption studies were done in a fixed bed adsorption system (height: 30 cm and inner diameter: 0.93 cm) as shown in Fig. S1. K-type thermocouple was used to measure the bed temperature along the column. About 2 g of adsorbent (length ~1 cm) was placed in the adsorption column with height of the packing ca. 22 cm and elevating the temperature to

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