



Carbon dioxide adsorption on nitrogen enriched carbon adsorbents: Experimental, kinetics, isothermal and thermodynamic studies



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ABSTRACT

Nitrogen enriched porous carbons were prepared by nanocasting method using hexamethoxymethyl-melamine (HMMM) as precursor and MCM-41 silica as template. Carbonization temperature was varied from 500 °C to 800 °C and was followed by physical activation with CO₂ at the same temperature. These materials were evaluated as adsorbents for CO₂ capture. Textural and morphological properties of these carbons show that they have mesoporosity derived from template removal. Carbonization and activation at 700 °C produced carbon with highest surface area of 463 m²/g and total pore volume of 0.48 cm³/g with nitrogen content of 9.2 wt%. Both of these properties account for the highest CO₂ uptake of 0.80 mmol/g at 30 °C using pure CO₂. CO₂ uptake decreased with increase in temperature suggesting occurrence of physisorption process. Additionally, these prepared carbons exhibited stable cyclic adsorption capacity. CO₂ adsorption kinetics on these adsorbents follow pseudo-first order model with maximum error of ca. 5.4%. The adsorbent surface was found to be energetically heterogeneous as suggested by Temkin isotherm model. Thermodynamics suggested exothermic, random and spontaneous nature of the process.

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1. Introduction

Climate change, a vital global problem at present, is the result of increasing anthropogenic carbon dioxide emissions. Combustion of fossil fuels, for meeting the world's energy requirements, contributes to a great extent to these emissions and they are expected to remain the primary energy source for this century [1–3]. Hence, there is a need to develop technologies that will allow the fossil fuel usage while reducing anthropogenic CO₂ emissions. Carbon dioxide capture and sequestration (CCS) appears to be a promising approach to mitigate increasing CO₂ levels. In addition, it will buy time for cost reduction of renewable energy sources while facilitating cleaner use of fossil fuels [4,5].

Separation of CO₂ based on adsorption seems to be a promising method in the field of CCS on account of its low equipment cost, low energy consumption and ease of application. Porous materials such as zeolites, carbons, metal-organic frameworks and amine supported silica have been evaluated as potential candidates for CO₂ separation from flue gas [6–11]. A time consuming post treatment by the use of corrosive and toxic reagents is required to

prepare amine supported zeolite and silica based adsorbents. Moreover, these adsorbents lack stability over various adsorption cycles and need to be regenerated at high temperatures for longer duration [7,12]. In comparison to these adsorbents, porous carbon based adsorbents offer several advantages such as large surface area, tunable porosity, high adsorption capacity, and ease of regeneration. They can be synthesized from large variety of low cost sources and by various techniques like sol-gel method, carbonization of carbon material and nanocasting. Among the techniques mentioned, nanocasting offers the development of carbon materials with controlled pore structure. In this process, a carbon precursor is infiltrated into the pores of the template and heat treated under controlled atmosphere. Then the template is removed by selective dissolution in hydrogen fluoride or sodium hydroxide. Pore structure of the prepared materials can be tailored depending on the template's pore structure [13,14]. Moreover, introduction of hetero atoms like nitrogen in the carbon matrix enhances its surface polarity and basicity thereby improving the interaction between acidic gas molecules like CO₂ and carbon surface [15,16]. Up till now, porous carbon adsorbents were mainly prepared by impregnation of basic amine groups after the synthesis of carbon material or by ammonia treatment but leads to instability of the amine and hence lacks the reusability of the

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adsorbent after consecutive adsorption runs [17,18]. Alternatively, nitrogen enriched carbon materials can also be prepared by using nitrogen containing monomers e.g. melamine, aniline etc. with the templates like zeolite and mesoporous silica [19–21]. Xu et al. [22] synthesized mesoporous carbon materials by using sucrose as precursor and nano-CaCO₃ as template and studied the effect of template to precursor ratio on textural properties. Nitrogen-doped porous carbon monoliths were produced by direct pyrolysis of the copolymer of resorcinol, formaldehyde, and lysine and they showed static CO₂ uptake of 3.13 mmol/g at 25 °C under pure CO₂ flow [18]. Pevida et al. [19] reported the synthesis of nitrogen enriched carbon adsorbents from melamine-formaldehyde resin having CO₂ uptake of 2.25 and 0.86 mmol/g at 25 °C and 75 °C respectively under pure CO₂ environment. In another work, nitrogen enriched carbons were prepared from urea-formaldehyde and melamine-formaldehyde resins and chemical activation with K₂CO₃ and they exhibited CO₂ uptake of 1.8 mmol/g and 1.03 mmol/g at 25 °C respectively [23]. However, it is important to note that most of the reported literature includes development of carbon adsorbents by direct carbonization and chemical activation of various raw materials followed by their CO₂ adsorption study under static flow conditions at room temperature, which does not have much relevance with respect to practical application in CO₂ capture. CO₂ capture performance under dynamic conditions is more important and the same has been carried out in this work.

In the present study, we report the preparation of mesoporous carbons by employing a novel nitrogen-rich polymer i.e. hexamethoxymethylmelamine (HMMM) resin as the carbon precursor with mesoporous silica as template. Carbonization temperature was varied from 500 to 800 °C to obtain a range of adsorbents. These adsorbents were evaluated for their textural, morphological and chemical properties followed by their dynamic evaluation as adsorbents for CO₂ capture. Also, static equilibrium adsorption capacities of pure CO₂ and N₂ on prepared adsorbents were also measured. Cyclic adsorption-desorption studies were carried out to check their stability followed by kinetic, isotherm and thermodynamic studies.

2. Materials and methods

2.1. Materials

Hexamethoxymethylmelamine (HMMM), procured from M/s Techno Waxchem Pvt. Ltd., India, was used as polymeric precursor. HMMM is methylated melamine-formaldehyde resin and is obtained from methylation reaction between melamine and formaldehyde followed by methylation with methanol under acidic conditions [24]. Mesoporous silica (MCM-41) having surface area of 450 m²/g and average pore diameter of 3.5 nm was purchased from M/s Tianjin Chemist Scientific Ltd., Tianjin, China and was used as hard template. Ethanol (100% pure), used as solvent, and sodium hydroxide pellets (A. R. grade) were purchased from M/s S. D. Fine Chemicals India Ltd. Dry nitrogen and carbon dioxide gases of 99.999% purity and special gas mixtures of CO₂ and N₂ were procured from M/s Sigma Gases and Services, India.

2.2. Adsorbent preparation

Carbon adsorbents were prepared by templating HMMM resin in the pores of mesoporous silica template followed by carbonization in N₂ and activation in CO₂ (each for 1 h) and then template removal as reported elsewhere [25]. In a typical procedure, around 80 g of HMMM resin was dissolved in pure ethanol followed by addition of 40 g of template (silica). This mixture was thoroughly mixed and then excessive solvent was removed by heating at

120 °C for 3 h to obtain templated resin. Carbonization of these templated resins was performed in a quartz tubular furnace by heating the samples at a rate of 10 °C/min up to 500–800 °C for 1 h under N₂ atmosphere. This was followed by physical activation with CO₂ gas [26,27] by switching the gas from N₂ to CO₂ for 1 h under isothermal conditions. After physical activation, gas was switched back to N₂ during cooling to room temperature to avoid excess gasification during cooling process. Template was removed by dissolution of samples in 40 wt% NaOH solution for at least 24 h and washing with excess amount of water. Samples were dried in oven at 100 °C for 3 h and were designated as C-T, where T denotes the carbonization temperature.

2.3. Adsorbent characterization

Elemental analysis (CHN) was performed using a Thermo Scientific Flash 2000 organic elemental analyzer (CHNS/O analyzer). Oxygen content was determined by difference. Kjeldahl method was also used to estimate the nitrogen content of the prepared adsorbents. Fourier transform infrared (FTIR) spectra of the prepared carbons were recorded on a PerkinElmer model 100 FTIR spectrometer in the wavelength range of 4000–625 cm⁻¹ with a resolution of 4 cm⁻¹.

Surface area and pore volume of the adsorbents were measured from nitrogen sorption isotherms at 77 K on a Micromeritics ASAP 2020 sorption analyzer. Prior to any measurement, samples were outgassed at 200 °C for 6 h under vacuum, to remove any gases or vapors that may have become physically adsorbed onto the adsorbent surface. Surface area (S_{BET}) was determined using the Brunauer-Emmett-Teller (BET) equation and the total pore volume (V_{total}) was calculated from amount of N₂ adsorbed at relative pressure of $P/P_o = 0.99$. Mesopore size distribution was derived from the Barrett-Joyner-Halenda (BJH) method while micropore size distribution was obtained from Horvath-Kawazoe (HK) method. Transmission electron microscopy images were obtained with a Philips Tecnai 20 transmission electron microscope using an accelerating voltage of 200 kV. To classify the surface functional groups present on the prepared carbon adsorbents, X-ray photoelectron spectroscopy (XPS) was carried out by means of a SPECS system using Mg K α X-ray source (energy 1253.6 eV). Both low and high resolution scans were carried out by using pass energies of 50 and 20 eV respectively.

Temperature programmed desorption (TPD) of CO₂ was carried out using a Micromeritics AutoChem II 2920 chemisorption analyzer equipped with a thermal conductivity detector. Carbon sample (ca. 100 mg) was first pretreated under pure He flow at 200 °C and then the temperature was decreased to 30 °C. Adsorption of CO₂ was conducted by switching gas from He to CO₂ for ca. 30 min. This was followed by desorption experiment by switching back to He gas and increasing the temperature to 250 °C.

2.4. Dynamic CO₂ capture performance

Thermo gravimetric analyzer (TA Q500, TA Instruments, US) was used to measure the CO₂ adsorption-desorption potential of the prepared carbon adsorbents at atmospheric pressure. In a typical experiment, ca. 20 mg of sample was loaded onto a platinum pan and temperature was raised from 30 °C to 200 °C, at a heating rate of 10 °C/min, under pure N₂ gas (flow rate = 50 ml/min) and held at this temperature for 2 h to remove any pre-adsorbed moisture. Temperature was then decreased to the desired adsorption temperature (i.e. 30 °C) and the gas was switched to pure CO₂ at a flow rate of 50 ml/min. On the complete saturation of the adsorbent, the gas flow was switched from CO₂ to N₂ and the temperature was increased to 200 °C to carry out desorption study. This adsorption-desorption cycle was repeated ten times. Among

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