



Synthesis of nitrogen enriched porous carbons from urea formaldehyde resin and their carbon dioxide adsorption capacity



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ABSTRACT

Carbon dioxide capture needs development of cost effective CO₂ capture technologies. This paper describes nitrogen enriched porous carbons synthesized from nanocasting technique using mesoporous silica as template and urea-formaldehyde resin as precursor. These carbon materials were evaluated as sorbents for CO₂ capture by using a thermogravimetric analysis under dynamic conditions. Carbonization and physical activation with CO₂ at different temperatures (500–800 °C) were carried out that resulted in the generation of different carbon adsorbents containing nitrogen functional groups. The textural characterization result reveals effect of nanocasting technique, which is confirmed from the generation of mesopores (0.644 cm³ g⁻¹), micropores (0.123 cm³ g⁻¹) and high surface area (337.07 m² g⁻¹) of adsorbent. The CO₂ capture capacity depends more on the nitrogen functionalities in addition to textural properties and nitrogen content, as the sample synthesized at 700 °C shows highest uptake capacity of 1.3 mmol g⁻¹. Furthermore, it was found that adsorbent can be easily regenerated, which was also seen by the lower value of isosteric heat of adsorption. Ten adsorption-desorption cycles show established materials' excellent stability as an adsorbent. Different kinetic models were fitted for the adsorption data and on the basis of correlation coefficient (R^2), fractional order provided best fit with the experimental data. The heterogeneous nature of the adsorbent surface was seen by best fitting of Freundlich isotherm and from the pattern of isosteric heat of adsorption. Exothermic, spontaneous and feasible nature was suggested by thermodynamic parameters' values. The thermal energy needed for desorption of CO₂ from the adsorbent surface was around 1.28 MJ per kg CO₂.

1. Introduction

Nowadays, world is facing tremendous challenges due to increase in greenhouse gas emissions (mainly carbon dioxide), which causes a major global warming problem. Its release into the atmosphere is mainly due to burning of fossil fuels such as coal, petroleum and natural gas [1,2]. It is expected that its concentration will get doubled by 2050, if no major actions are taken [3]. Various methods are available to reduce CO₂ emission in the atmosphere such as geo-engineering approaches, afforestation and reforestation, carbon dioxide capture & sequestration (CCS) system and by using renewable energy sources and increased usage of low carbon fuels [4–7]. Its capture & sequestration (CCS) has drawn much global attention.

The available CCS technologies to capture CO₂ are absorption, adsorption [8], cryogenic processes [9], and membrane separation. In this respect, mature technologies like gas absorption by alkanamines solutions have been used maximum for CO₂ scrubbing on industrial scale. However, they have several shortcomings such as inherent regeneration

cost and inefficiency [10]. Therefore, there is a need to find an alternative route. In contrast, it is widely recognized that adsorption by porous adsorbents is attractive because of its low energy consumption and higher adsorption capacity [11,12]. Current research activities are focused on carbon based adsorbents [13], zeolites [14,15], mesoporous silica material SBA-15 [16], and amine-enriched sorbents to separate CO₂ from fossil fueled power plants. Some of them also tried to improve uptake capacity and selectivity of adsorbents through amine modification, but they faced problems like poor stability and blocking of adsorbent pores. Therefore, carbon based adsorbents are found to be attractive among them due to its high surface area, lesser amount of energy for regeneration, good thermal/mechanical stability and hydrophobicity [17]. Three methods are available for the synthesis of carbon materials: (a) carbonization and activation of carbon containing precursor, (b) sol gel process and (c) nanocasting method [18–20]. By using first two methods (sol gel and carbonization followed by activation), mesoporous carbons with somewhat tunable properties can be developed. But it is not possible with this method to develop adsorbents

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with controlled pore structure characteristics. However, this can be possible by nanocasting method which is performed in this study [21]. It is possible to develop adsorbents with better textural properties. Also, it has been reported in literature that to increase the adsorption capacity of the adsorbent, heteroatoms like nitrogen and oxygen play an important role in improving its surface property. This was due to the modification which causes an increase in active sites like Lewis base, helping in CO₂ capture [22].

Hao et al. [23] successfully prepared nitrogen doped porous carbon monoliths through direct pyrolysis of copolymer of resorcinol and formaldehyde resins under L-lysine as catalyst which exhibited CO₂ uptake of 3.13 mmol g⁻¹ at 25 °C and 100% CO₂ flow under static conditions. Drage et al. [24], by using urea-formaldehyde and melamine-formaldehyde resins, developed nitrogen rich carbons which exhibited CO₂ uptake up to 1.86 and 1.03 mmol g⁻¹ at 25 °C at 1 atm under pure CO₂ flow. Zhen et al. [25] reported nitrogen doped carbon prepared from urea-formaldehyde resin co-polymerized with furfuralcohol which exhibited a static CO₂ uptake capacity of 3.76 and 1.57 mmol g⁻¹ at 25 °C and 75 °C, respectively.

It was seen that many researchers were trying to develop adsorbent either by direct carbonization or by physical/chemical activation. Also, they tried to evaluate their uptake capacity mainly under static condition at room temperature. But, the disadvantage of their studies is both the synthesis and performance evaluation. It was reported that direct carbonized adsorbent synthesis was time consuming and requires high amount of energy. Moreover, evaluation of adsorbent carried under static condition gives higher value of uptake capacity and it will not provide the real picture for flue gas applications. To overcome this gap, this study has been conducted in which nanocasting technique was used to improve textural properties of adsorbent and performance evaluation under dynamic conditions at different CO₂ concentrations (6–100%) and temperatures (30–100 °C), which is more important than static conditions. Regenerability, kinetics, adsorption isotherm, thermodynamics and energy calculations studies have also been conducted in this study.

2. Experimental section

2.1. Materials

Mesoporous silica having a pore diameter of 3 nm and surface area of 800 m² g⁻¹ was utilized as a template and purchased from M/s Tianjin Chemist Scientific Ltd, China. Sodium hydroxide pellets, formaldehyde solution (37–41 wt.%) and urea were purchased from M/s S. D. Fine Chemicals Ltd., India. Here, urea was selected because it contains a large amount of nitrogen and it was also easily available, which fulfills one of the ideal adsorbent characteristics of easy availability at low cost. High purity nitrogen gas (99.995%), carbon dioxide gas (99.999%) and gas mixtures (6%, 20% and 50% CO₂ rest nitrogen) used in this study were provided by M/s Sigma Gases and Services, India.

2.2. Preparation of adsorbents and activation procedure

Urea (224 g) was added to the solution of formaldehyde (600 ml, 37% w/v) followed by stirring for 30 min. To this, 1 N NaOH solution was added to adjust the pH of the solution to 9. The solution was heated to 80–85 °C for 2 h. Further, cooling was done to 55 °C followed by the addition of sulfuric acid to maintain the pH to 5–5.5. Further, the temperature was increased to 85–90 °C and maintained at this temperature for the next 1 h and then cooled. Next, template (57 g) and sulfuric acid were added to this solution and mixed until it became homogenous suspension. To ensure complete dryness, templated resin was kept in the oven for 3 h at 120 °C.

Carbonization-activation of the templated resin was carried out in a tubular furnace under N₂ or CO₂ flow at 500–800 °C at 10 °C min⁻¹ to generate a range of adsorbents. Gas flow of 60 ml min⁻¹ was

maintained throughout the experiment. Carbonization under nitrogen atmosphere and activation under carbon-dioxide atmosphere have been performed for 1 h each. CO₂ activation was performed for gasification of carbon adsorbents and to improve their textural properties. After completion of this, switching of gas from carbon dioxide to nitrogen at a flow rate of 60 ml min⁻¹ was done. The template was subsequently removed by dipping the sample in NaOH solution for 48 h followed by washing with copious amount of distilled water. After this, the sample was kept in the oven at 100 °C for complete drying. The resultant samples were denoted as UFZ-T where T is carbonization and activation temperature. To study the effect of nanocasting technique, a reference sample was also prepared at 700 °C by direct carbonization and denoted as UF-700.

2.3. Adsorbent characterization

The surface morphology of the adsorbent was examined by scanning electron microscopy (Model-JEOL JSM – 6510 LV scanning electron microscope equipped with electron dispersive x-ray analysis (EDS) facility). The instrument was operated at an accelerating voltage of 20 kV. Before analysis, sample was coated with gold to prevent sample charging problems. Raman spectra of the samples before and after CO₂ adsorption were obtained using a confocal Raman microscope (WITec alpha 300R, Germany) with $\lambda = 532$ nm laser excitation to evaluate any structural changes occurring in the adsorbent due to adsorption of CO₂. It was also used to examine the presence and position of D-(disordered) and G-(graphitic) peak and their intensity ratio. TEM images of samples were recorded on a Philips CM-200 transmission electron microscope operated at 200 kV. Nitrogen adsorption/desorption isotherms were obtained at 77 K using a Micromeritics ASAP 2010 sorption analyzer. Before measurements, the samples were degassed at 200 °C for at least 6 h to remove physically adsorbed gases from the adsorbent surface. The surface area was calculated using the Brunauer-Emmett-Teller (BET) method. The pore size distributions (PSDs) were obtained using Barrett-Joyner-Halenda (BJH) model and total pore volume from N₂ adsorption data in the relative pressure range of $P/P_0 = 0.99$. X-ray photoelectron spectroscopy (XPS) measurements were made to identify nitrogen and oxygen moieties on carbon adsorbents using Kratos axis ultra DLD system with a monochromated Al K α source operated at 15 kV. Pressure of 2×10^{-9} torr was maintained in the analysis chamber. Data processing was performed using the XPS peak 4.1 software.

2.4. CO₂ adsorption measurements

Dynamic adsorption/desorption was done by placing 20 mg of adsorbent on platinum pan of thermogravimetric analyzer (TA Q500, TA Instrument, USA) and pretreated under N₂ flow (50 ml min⁻¹) at 200 °C for 2 h to remove moisture adsorbed in the adsorbents. After pretreatment, the temperature was reduced to a desired adsorption temperature (30, 50, 75, 100 °C) followed by switching of gas flow from N₂ to pure CO₂ or mixture of CO₂ and N₂ (6%, 20%, 50% CO₂ balance N₂) at 50 ml min⁻¹ to perform the adsorption study.

2.5. Sorbents regeneration

The adsorbent regeneration was done by heating the sample to 200 °C at 10 °C min⁻¹ under N₂ flow (50 ml min⁻¹) after completion of the adsorption experiment and by maintaining at 200 °C for 2 h. To check the adsorbent stability for a long time, the adsorption/desorption procedure was repeated ten times.

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