



Research article

Development of chemically activated N-enriched carbon adsorbents from urea-formaldehyde resin for CO₂ adsorption: Kinetics, isotherm, and thermodynamics

Deepak Tiwari, Haripada Bhunia*, Pramod K. Bajpai

Department of Chemical Engineering, Thapar Institute of Engineering & Technology (Deemed to be University), Patiala 147004, Punjab, India

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ABSTRACT

Nitrogen enriched carbon adsorbents with high surface areas were successfully prepared by carbonizing the low-cost urea formaldehyde resin, followed by KOH activation. Different characterization techniques were used to determine the structure and surface functional groups. Maximum surface area and total pore volume of 4547 m² g⁻¹ and 4.50 cm³ g⁻¹ were found by controlling activation conditions. The optimized sample denoted as UFA-3-973 possesses a remarkable surface area, which is found to be one of the best surface areas achieved so far. Nitrogen content of this sample was found to be 22.32%. Dynamic CO₂ uptake capacity of the carbon adsorbents were determined thermogravimetrically at different CO₂ concentrations (6–100%) and adsorption temperatures (303–373 K) which have a much more relevance for the flue gas application. Highest adsorption capacity of 2.43 mmol g⁻¹ for this sample was obtained at 303 K under pure CO₂ flow. Complete regenerability of the adsorbent over four adsorption-desorption cycles was obtained. Fractional order kinetic model provided best description of adsorption over all adsorption temperatures and CO₂ concentrations. Heterogeneity of the adsorbent surface was confirmed from the Langmuir and Freundlich isotherms fits and isosteric heat of adsorption values. Exothermic, spontaneous and feasible nature of adsorption process was confirmed from thermodynamic parameter values. The combination of high surface area and large pore volume makes the adsorbent a new promising carbon material for CO₂ capture from power plant flue gas and for other relevant applications.

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1. Introduction

Increasing concentration of anthropogenic carbon dioxide (CO₂) in the atmosphere due to combustion of fossil fuels is the major cause of global climate deterioration. Its concentration has reached to a level of 408.84 ppm (Earth's CO₂, 2018) according to current scenario and is expected to increase up to a level of 570 ppm by 2100 (Yu et al., 2008). Currently, carbon dioxide capture and storage from fixed point sources is the prevailing strategy to reduce carbon dioxide in the atmosphere (Tiwari et al., 2017a; b). In this respect, on a large scale, amine absorption technology using monoethanol amine and alkanolamine is well-tried technology (Chatti et al., 2009) but this technology suffers from several drawbacks e.g., equipment corrosion, high energy consumption and environmental

problems. Therefore, there is a great need to develop alternative capture technology. Adsorption technology is another promising and cost effective route which offers several advantages over absorption technology such as mild operating conditions and low energy consumptions (Siriwardane et al., 2001). However, high adsorption capacity, outstanding cycling performance and high CO₂/N₂ selectivity are the key essentials for temperature and pressure swing adsorption technologies (Liu et al., 2014). Large variety of porous adsorbents have been tested like zeolites (Khelifa et al., 2004), porous carbons (Sevilla and Fuertes, 2011), amine modified materials (Chatti et al., 2009), covalent-organic-frameworks (COFs) (Abid et al., 2012) and metal-organic-frameworks (MOFs) (Patel et al., 2012) for CO₂ adsorption.

Compared with other materials, carbonaceous adsorbents possess unique superiority such as low-cost, high stability, high hydrophobicity, low energy requirement for regeneration and tunable pore structure (Liu et al., 2015). Recently, researchers have focused on enhancing adsorption capacity and selectivity of carbon materials using nitrogen, oxygen etc. as a heteroatoms and by

* Corresponding author.

E-mail addresses: deepak.tiwari@thapar.edu (D. Tiwari), hbhunia@thapar.edu (H. Bhunia), pramod.iitk77@gmail.com (P.K. Bajpai).

developing fine micro-pores. Hao et al. (2010) prepared nitrogen-doped porous carbon monoliths by pyrolysis of copolymer of resorcinol, formaldehyde and lysine. The static CO₂ adsorption capacity was 3.13 mmol g⁻¹ at 298 K under pure CO₂ atmosphere. High nitrogen content carbon adsorbents prepared by Goel et al. (2015) from melamine-formaldehyde resin showed CO₂ uptake of 0.792 mmol g⁻¹ at 303 K under 100% CO₂ flow. In another work, Tiwari et al. (2017a; b) using precursor melamine and carbonization followed by physical activation with CO₂ developed N-enriched carbon which shows CO₂ uptake of 0.93 mmol g⁻¹ at 303 K. This study concluded that both surface area and nitrogen functional groups have a major impact on adsorption capacity. High nitrogen content carbons synthesized by Liu et al. (2014) using urea-formaldehyde and chemical activation with KOH showed static CO₂ uptake of 3.21 mmol g⁻¹ at 298 K. This study shows that in addition to microporosity, heteroatoms also to be considered as important factor in CO₂ adsorption performance. Nitrogen enriched carbon material was synthesized by Wang and Yang (2011) using CVD process and zeolite as a template having CO₂ adsorption capacity of 3.1–4.4 mmol g⁻¹ at 298 K and 1 bar. Wickramaratne and Jaroniec (2013) synthesized phenolic resin based carbon materials which exhibited CO₂ uptake of 4.6 mmol g⁻¹ at 297 K. However, for the preparation of above sample of high adsorption capacity, carbon sourcing is expensive and synthesis process is complicated. Also, the nitrogen content achieved was below 7 wt%, which is believed to be not good for CO₂ adsorption capacity and CO₂/N₂ selectivity point of view, as the N₂ concentration has an appreciable effect. Direct carbonization of nitrogen containing polymer precursors such as melamine suffers from the disadvantage of having poor porosity (Tiwari et al., 2017a; b) resulting in low adsorption capacity. Therefore, carbonization followed by activation by using appropriate activation conditions and carbon sources or templating method is necessary to improve the porosity of carbon adsorbents. Urea as a carbon and nitrogen source is more effective because of its cost and availability which is used in the present study. So far, very few studies have been reported on this for the development of carbon adsorbents by activation method for CO₂ adsorption. Drage et al. (2007) obtained carbon materials by using melamine-formaldehyde (MF) and urea-formaldehyde (UF) resins as precursor and chemical activation by K₂CO₃. The CO₂ adsorption capacity of MF based sample was 1.03 mmol g⁻¹ and for UF based sample, it was 1.8 mmol g⁻¹ at 298 K. Nitrogen rich carbons, prepared by Liu et al. (2014) from urea-formaldehyde by chemical activation with KOH, exhibited adsorption capacity of 3.21 mmol g⁻¹ at 298 K under static condition. In these studies, performance evaluation has been carried out under static conditions at 273–303 K, which has not much relevance from the flue gas application point of view.

In the present work, cost-effective and largely available precursor was used to prepare carbon adsorbents using chemical activation with KOH. The conditions were optimized for the parameters such as KOH:UF ratio, activation time and activation temperature. The carbon adsorbents were thoroughly characterized using various techniques like N₂ adsorption/desorption, SEM, TEM, elemental analysis, FTIR, XPS, TGA and TPD. Performance evaluation of the adsorbents under dynamic condition, which is more relevant from flue gas point applications, was carried out thermogravimetrically at different CO₂ concentrations (6–100%) and at different adsorption temperatures (303 to 373 K). Regenerability, kinetics, adsorption isotherm, and thermodynamics have also been studied.

2. Experimental

Urea, formaldehyde solution (37–41 wt %), potassium hydroxide (KOH) used in this study were supplied by M/s S.D. Fine Chemicals

Ltd., India. Nitrogen gas (99.995%), carbon dioxide gas (99.999%) and gas mixtures used in this study were supplied by M/s. Sigma Gases and Services, India.

2.1. Preparation of adsorbents

For synthesis of UF, 224 g urea was added to 600 ml of 37% w/v formaldehyde solution in a 1000 ml three-necked round bottom flask equipped with stirrer, condenser and a thermometer, and was allowed to mix for 30 min with continuous stirring accompanied by addition of 1 N NaOH to adjust the pH of the solution to 9. Next, the temperature was raised to 353–358 K for heating of solution for 2 h and was allowed to cool up to 328 K. To this solution, sulfuric acid was added to adjust the pH to 5–5.5. Temperature of solution was again raised to 358–363 K and maintained for 1 h. Solution was then cooled to 318 K, followed by the addition of sulfuric acid. The obtained sample was completely dried for 3 h at 393 K. Fig. S1 presents the block diagram of preparation of UF resin.

The obtained sample was carbonized in a tubular furnace and heated to 973 K at a heating rate of 10 °C min⁻¹ followed by maintaining the isothermal condition for 2 h. N₂ gas flow of 60 ml min⁻¹ was maintained throughout the experiment. The obtained carbonized material was denoted as UF-973 and was taken as reference sample for this study. The block diagram of adsorbent preparation is shown in Fig. S2.

2.2. Chemical activation

For chemical activation of sample (UF-973), potassium hydroxide (KOH) was used. UF-973 was thoroughly mixed with KOH at the desired weight ratio of (KOH:UF = 1–4:1). The resulting mixture was dried at 378 K for 12 h. The dry material was placed in a tubular furnace, followed by heating to a predetermined activation temperature ranging from 773 K to 1073 K at 10 °C min⁻¹ heating rate in N₂ flow of 60 ml min⁻¹. After, cooling to room temperature, it was washed with 1 M HCl and distilled water until the neutral pH was obtained. This was done to remove the chloride ions also. Finally, the activated samples were dried in oven at 393 K. The obtained materials are listed in Table 1 with sample notation and preparation variable. Fig. S3 presents the block diagram of activation process.

2.3. Adsorbent characterization

Nitrogen adsorption-desorption isotherms at 77 K were obtained using a Micromeritics ASAP 2010 sorption analyzer. Before measurement, the degassing of the samples was performed for 6 h at 493 K to remove the moisture and physically adsorbed gases from the adsorbent surface. The specific surface area (S_{BET}) was calculated by using the Brunauer-Emmet-Teller (BET) method. The total pore volume (V_{total}) was estimated from the amount of N₂

Table 1
Samples prepared at various conditions.

Samples notation	Carbonization temperature (K)	Activation temperature (K)	KOH:UF (mass ratio)
UF-973	973	–	–
UFA-1-973	973	973	1
UFA-2-973	973	973	2
UFA-3-973	973	973	3
UFA-4-973	973	973	4
UFA-3-773	973	773	3
UFA-3-873	973	873	3
UFA-3-1073	973	1073	3

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