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Research article

Melamine-formaldehyde derived porous carbons for adsorption of CO_2 capture

Deepak Tiwari [a], Chitrakshi Goel [a, b], Haripada Bhunia [a, *], Pramod K. Bajpai [a]

[a] Department of Chemical Engineering, Thapar University, Patiala 147004, Punjab, India
[b] Ghent University – Laboratory for Chemical Technology, Technologie park 914, B-9052 Ghent, Belgium

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ABSTRACT

In this work, we report carbon adsorbents obtained from high nitrogen content melamine-formaldehyde resin as starting material and mesoporous zeolite MCM-41 as template through nanocasting technique. To synthesize different carbon structure adsorbents with improved textural and surface properties, the material undergo carbonization followed by physical activation under CO_2 atmosphere at different temperatures. Characterizations of the adsorbents using SEM, TEM, XPS, nitrogen sorption, CHN, TKN, and TPD have been carried out. Characterization results reveal the development of nanostructured carbon adsorbents with better texture and surface properties as compared to the sample prepared by direct carbonization. Sample prepared at carbonization-activation temperature of 700 °C shows highest basicity, surface area (193.28 $m^2\ g^{-1}$) and pore volume (0.32 $cm^3\ g^{-1}$). Performance evaluation of adsorbent was performed thermo gravimetrically at different temperatures and concentrations and was found that the adsorbent synthesized at 700 °C exhibit highest CO_2 uptake of 0.93 mmol g^{-1} with nitrogen content of 22.73%. It was found that both surface area and nitrogen functional group have a major impact on adsorption capacity. Physiosorption process was confirmed by a decrease in adsorption capacity with increase in temperature. Three kinetic models and isotherms were used in this study and found that fractional order kinetic model and Freundlich isotherm best fitted with the experimental data. Isotherm study depicts the heterogeneous nature of adsorbent surface. Adsorbent exhibited complete regenerability and was stable over four adsorption-desorption cycles. Low value of isosteric heat of adsorption of 15.75 kJ mol^{-1}, indicates physiosorption process. Negative value of ΔG^0 and ΔH^0 confirms spontaneous, feasible and exothermic nature of adsorption process.

1. Introduction

Global warming caused by increasing CO_2 concentration in the atmosphere is the major current challenging issue. The increase in CO_2 concentration is due to burning of fossil fuel such as coal, natural gas or petroleum etc. Its concentration has increased from 280 ppm to 406.67 ppm at present (2017) and it is expected to rise up to a level of 550 ppm by 2100 (Tiwari et al., 2016a, 2016b) as the fossil fuels will continue to be the major source of energy. Increase in concentration of CO_2 at this rate will harm the global environment and will create problem like drought, global surface temperature rise, and increase in acidity of sea level. Therefore, there is a need to reduce anthropogenic CO_2 emissions by capturing CO_2 with inexpensive adsorbents (Lu and Schüth, 2006).

Some of the adsorbents tested by different research groups are activated carbon (Siriwardane et al., 2005), zeolites (Wahby et al., 2010), mesoporous silica material SBA-15, MCM-41 (Sun et al., 2015), and amine-enriched sorbents (Himeno et al., 2005). But the problems like corrosion, high energy requirement for regeneration, lack of adsorption stability are still there. An ideal adsorbent should have the characteristics of high adsorption capacity, low energy requirement for regeneration, cost effective, stable over multiple cycles and high surface area (Hornbostel et al., 2013).

Recent studies show that carbon adsorbents fulfill the above criteria and can be easily prepared by various technologies like nanocasting, direct carbonization of precursor and sol-gel process (Hornbostel et al., 2013; Karandikar et al., 2007). Among these methods, adsorbent prepared by nanocasting technology is very

* Corresponding author.
E-mail addresses: Deepak.tiwari@thapar.edu (D. Tiwari), chitrakshigoel@yahoo.co.in (C. Goel), hbhunia@thapar.edu (H. Bhunia), pramod.iitk77@gmail.com (P.K. Bajpai).

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effective and simple which involves infiltration of the precursor into the pores of hard template, followed by carbonization and template removal. This technology is helpful in increasing surface area and porosity development which is not possible by direct carbonization. Very few studies have been reported on this technology (Valdés-Solís and Fuertes, 2006). Also to increase the adsorption capacity of the adsorbent, different functional groups (acidic) are incorporated on the surface of adsorbent which will increase its affinity towards Lewis basic CO_2 molecules (Przepiórski et al., 2004).

(Hao et al., 2010) reported CO_2 uptake of nitrogen doped carbons synthesized and modified under amino acid L-lysine as a catalyst from direct pyrolysis of resorcinol and formaldehyde. The modified adsorbent shows CO_2 uptake to be 3.13 mmol g^{-1} at 25 °C at 1 atm.

(Drage et al., 2007) reported CO_2 adsorption capacity of synthesized nitrogen enriched carbons from urea-formaldehyde and melamine–formaldehyde resins. The adsorbents undergo post synthesis treatment *i.e.* chemical activation under K_2CO_3. The synthesized adsorbents exhibit CO_2 uptake of 1.86 mmol g^{-1} at 25 °C under 100% CO_2 atmosphere.

Review of literature shows that adsorbents were mainly prepared by direct carbonization followed by physical or chemical activation and performance evaluation was done under static condition largely at 0 °C or 30 °C. The synthesis process i.e. direct carbonization followed by post synthesis treatment, is time consuming and required large energy and the adsorption capacity obtained under static condition gives higher value but will not give the real picture from CCS point of view. Performance evaluation carried out under dynamic condition will provide a better scenario which has been performed in this study. Therefore, synthesis of high nitrogen content mesoporous adsorbent has been developed in this study by nanocasting technique which will fulfill the characteristics of an ideal adsorbent. It will help in enhancing textural and surface properties of the adsorbent, which is not possible by the adsorbent synthesized by direct carbonization. Also to fulfill a gap of literature, performance evaluation of these adsorbents was conducted under dynamic conditions at various temperatures and at different CO_2 concentrations. More importantly, to check the performance of adsorbent for long term use, regeneration studies were conducted and found that this adsorbent shows easy regenerability and stability over multiple cycles. Detailed studies of kinetics, isotherm and thermodynamics were also performed.

2. Experimental

2.1. Materials

Nitrogen (99.995%), high purity carbon dioxide gas and a standard mixture of CO_2 and N_2 (6%, 20%, 50% v/v) were supplied by M/S. Sigma Gases Services, India. Template used in this study was mesoporous MCM-41 zeolite having a pore diameter of 3 nm and surface area of 800 m^2 g^{-1}, respectively. It was supplied by M/s Tianjin Chemist Scientific Ltd. Other chemicals used in this study were purchased from M/s S. D. Fine Chem. Limited and is of analytical grade.

2.2. Sample preparation

The adsorbents were synthesized by using precursor 46.6 g (melamine) and 200 ml of methanol (5 wt % solution) which was added in three neck round bottom flask, stirred and heated to about 70 °C. To this solution, 200 ml of formaldehyde solution (37% w/v) was added slowly for 3 h to generate hexamethylomelamine. To maintain the pH of the solution to 8–9, potassium carbonate was added and heated to 75 °C for advanced polymerization. Stirring was continued for the next 2 h. After this, 0.4 g of di-sodium tetra borate and N/10 sodium hydroxide solution were added. This helps in maintaining the pH of solution around 7–8. To this solution, 6 ml of sulfuric acid (48% v/v) and mesoporous zeolite (15 g) were added and mixed until homogenous suspension appears. Next, curing was performed for 2 h at 60 °C. This cured resin has undergone carbonization and physical activation, which was performed in a quartz tubular furnace by raising the temperature of the furnace to 500–800 °C at 10 °C min^{-1}. The carbonization was carried for 1 h under nitrogen flow and activation under carbon dioxide atmosphere for 1 h. Constant flow of 60 ml min^{-1} was maintained throughout. Switching of gas was done after activation from CO_2 to N_2 and allowed for cooling of furnace to avoid excess gasification. The final product was dissolved in 40 wt % NaOH solution for 48 h for removing the template. Then the samples were washed with distilled water several times, dried at 100 °C to remove the template. The obtained sample was denoted as MFZ-x where x is carbonization and activation temperature. Also for comparison of the results a reference sample was prepared by direct carbonization and denoted as MF-700. The block diagram for overall synthesis procedure of the adsorbent is shown in Fig. 1.

2.3. Characterization of the samples

The surface morphology of the samples was characterized by means of SEM (Model JEOL JSM – 6510 LV). Transmission electron microscopy (TEM) images were taken with a Philips CM-200

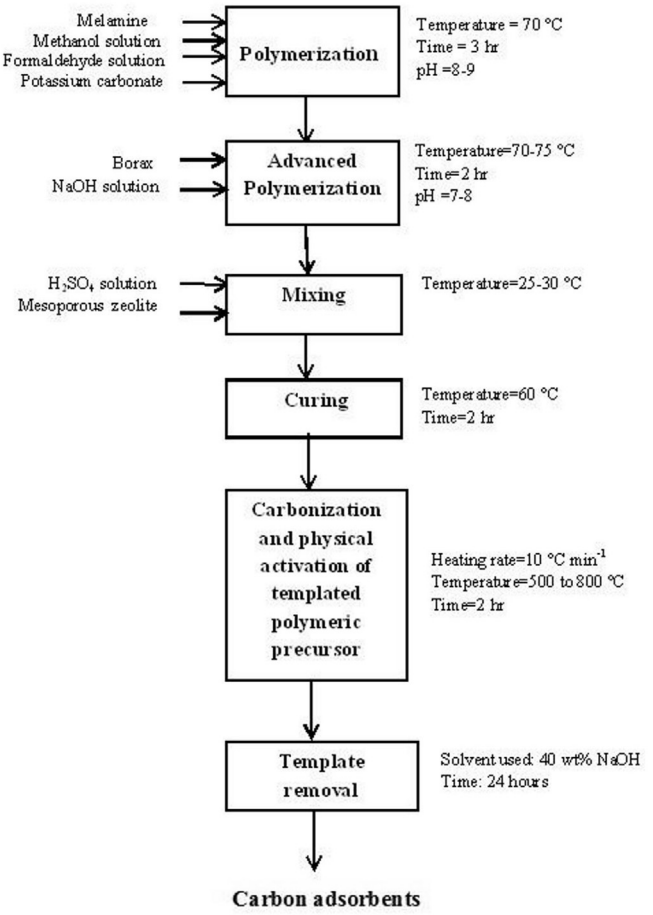

Fig. 1. Block diagram of the preparation method of nitrogen-enriched carbon adsorbent by nanocasting technique.