STUDIES ON CARBOHYDRATE DERIVED SORBENTS FOR CARBON DIOXIDE REMOVAL

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by

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ABSTRACT

Global Warming is the increase in the average temperature of Earth due to increased emission of greenhouse gases, which absorb the heat that would otherwise escape from the Earth surface. CO_2 is the primary anthropogenic greenhouse gas. During the past few decades, much effort has been committed for the development of new CO_2 capture materials. Adsorbents for CO_2 employ one of the two possible adsorption mechanisms, either chemical adsorption or physical adsorption. In chemisorptions, CO_2 undergoes a covalent chemical reaction to bind CO_2 to certain sites on the sorbent with a much greater heat of adsorption. In physisorption, CO_2 is adsorbed to the solid support by either van del Waals force of attraction or pole-pole interaction.

Recently, much attention has been given to the use of biomass to produce functional materials in terms of economic, environmental and societal issues. Biomass, because of its low cost, huge amount, easy access and environmental friendship has increased demand as a raw material for CO_2 adsorbent. The focus of research work is on the development of different CO_2 adsorbents from biomass.

In the thesis work, regenerable CO_2 capture materials are prepared using different carbohydrates as the raw materials. Three types of CO_2 capture materials were developed viz,. amine on solid support, microporous carbon and nitrogen-doped microporous carbon. These materials were evaluated for CO_2 adsorption capacity, recycle stability, selectivity etc.

Carbon dioxide adsorption on the supramolecular system of aniline encapsulated into β-cyclodextrin (β-CD) cavity is studied for the first time. Molecular level distribution of amine on solid support is achieved. Amine group of aniline oriented towards the wider rim of β-CD cavity is favourably exposed to the gas stream, which results in its maximum utilization for CO_2 capture. CO_2 adsorption capacity of 0.70 mmol/g (3.1 wt.%) and amine efficiency of 0.85 mol CO_2 adsorbed / mol of nitrogen in the adsorbent is observed for this system at ambient temperature and pressure. The mechanism of the chemisorption is through the formation of bicarbonate confirmed by NMR, Raman spectroscopy and molecular modelling studies. The heat of adsorption value from the DSC is -94 kJ/mol, which compares well with that for chemisorption of CO_2. The pseudo-second order rate equation is used to describe the chemisorptions of β-CD – aniline complex.

Microporous carbon nanospheres are prepared from β-cyclodextrin by solvothermal carbonization in o-dichlorobenzene in presence of various concentrations of p-toluene sulfonic acid (PTSA). The contribution of PTSA towards solvothermal char (STC) is established. The STC shows the highest surface area, porosity and CO_2 sorption capacity at a PTSA to β-CD weight ratio of 2.5. The surface area, pore volume and CO_2 sorption capacity are further increased by an in situ high temperature activation, due to the oxidation of carbon at high temperature by the oxygen present in the STC. The high temperature activation reduces the significance of PTSA concentration, as the activated STC showed surface area, micropore volume and CO_2 adsorption capacity in a close range at the PTSA to β –CD weight ratio in the range of 0.04 to 2.5. The highest CO_2 adsorption capacity increase from 2.4 to 3.5 mmol/g (10.6 to 15.4 wt. %) up on the high temperature activation. The activated STC adsorbs significant amount (0.35 mmol/g, i.e., 1.5 wt. %) of CO_2 from dry air containing 400 ppm CO_2.

More economical and acceccible raw mateial cotton is selected for the preparation of porous carbon. Microporous carbonaceous materials were developed by the solvothermal carbonization of natural cotton for the first time. Morphology and surface area of solvothermal char (STC) depend on the p-toluene sulfonic acid (PTSA) catalyst concentration. STC shows maximum surface area of 477 m^2/g, pore volume of 0.60 cm^3/g and CO_2 sorption capacity (at 25 °C and 1 bar) of 1.3 mmol/g (5.7 wt %). STC shows the same adsorption capacity when tested with pure CO_2 gas at 25 °C for several adsorptions-desorption cycles. High CO_2 uptake of 4.6 mmol/g (20.2 wt. %) at ambient temperature and 20 bars is exhibited by STC. STC-0.04 (prepared at PTSA to cotton weight ratio of 0.04) showed superhydrophobic character due to the nano projections on the fiber surface produced by heterogeneous nucleation of STC particles. STC-0.04 is an excellent sorbent for organic solvents from water.

Nitrogen enriched carbon with well-developed microporosity and superior CO_2 adsorption capacity are prepared by KOH activation of a nitrogen-containing polymer obtained by heating sucrose and urea. The nitrogen content, microporosity and surface area of the activated carbon depend on the concentration of urea and KOH. The maximum surface area, total pore volume and nitrogen content of the activated carbon achieved are 2366 m^2/g, 1.16 cm^3/g and 10.5 wt.%, respectively. A maximum CO_2 adsorption capacity of 7.0 mmol/g (30.8 wt. %) is achieved at 0^{o}C and 1 bar pressure. The CO_2 adsorption capacity of 0.70 mmol/g (3.1 wt. %) from dry air containing 400 ppm CO_2 achieved is the highest reported in the category of carbonaceous materials. The CO_2 adsorption capacity of all prepared carbon materials is well correlated with the nitrogen content and microporosity. The CO_2 adsorption on activated carbon materials shows excellent selectivity over N_2, with one of the highest selectivity factor of 38, hence an ideal candidate for CO_2 removal.