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Investigation of CO_2 adsorption on carbon material derived from *Mesua ferrea* L. seed cake

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ABSTRACT

In recent times, synthesis of valuable carbon materials via hydrothermal carbonization technique using biomass precursors for various applications has received revived interest in view of energy efficiency and sustainability. In present work, low-cost carbon material was synthesized using *Mesua ferrea* L. seed cake through hydrothermal carbonization method. The material was characterized using various techniques and its CO_2 capture performance was investigated through a dynamic column breakthrough measurements. The sorbent exhibited a fresh adsorption capacity of 2.63 mmol g^{-1} at 30 °C under a total pressure of 1 bar. Both textural properties and surface chemistry influence the CO_2 dynamic adsorption. The sorbent maintained an average working capacity of $\sim$ 2.47 mmol g^{-1} during eight cycles of adsorption-desorption. The experimental data can be adequately described by Yoon-Nelson kinetic model. The adsorption kinetic mechanism is further explained by applying intraparticle diffusion model to the experimental data.

1. Introduction

The economical synthesis of valuable carbon materials using diverse precursors has received much attention due to widespread application of these materials in separation, energy conversion, and catalysis. Particularly, there has been a plethora of research on synthesis of activated carbon (AC) using agricultural residues (straw, shell, husk, fruit peel, etc.), animal wastes (cow dung, sheep dung), and liquid fractions obtained from the thermal treatments of plant wastes and coals [1,3,12,33]. Physical (thermal) activation and chemical activation are the two well-established techniques for synthesis of AC. In physical activation, precursor is carbonized in the temperature range of 400–850 °C under inert atmosphere followed by activation using CO_2, NH_3, steam or air at around 600–900 °C. Chemical activation involves heating the mixture of precursor and dehydrating agent or oxidant, normally at a temperature less than 600 °C. The various chemicals used for activation include KOH, NaOH, K_2CO_3, H_3PO_4, H_2SO_4, HCl, and $ZnCl_2$ [20,23,28,32,38]. However, these techniques are energy intensive due to severe reaction conditions. Further, until recently, a little attention was paid to synthesize other types of carbon materials using biomass residues. Of late, there has been a revived interest in the synthesis of carbon materials using renewable sources through hydrothermal carbonization (HTC) [2,8,11,35,36,40]. Being environmentally benign and sustainable technique, HTC involves thermal treatment of an aqueous dispersion of precursor in an autoclave, either in the presence or in the absence of catalyst under mild conditions (around 200 °C temperature and self-generated pressure) [34].

The primary objective of the present work is to explore the applicability of carbonaceous material, obtained from *Mesua ferrea* L. seed cake using HTC technique, as a CO_2 adsorbent to be used in carbon capture and storage (CCS) technology. *Mesua ferrea* L. (Iron wood tree), member of Calophyllaceae family, is a canopy tree, which grows naturally in tropical evergreen forests of South Asian countries including India and Sri Lanka. Further, it is cultivated in

the gardens and avenues for its attractive flowers and foliage [24]. The seeds of *Mesua ferrea* L. tree, containing 60–63% extractable oil, were found to be promising precursors for non-edible oil based biodiesel production [6,25]. Seed cake is the by-product of biodiesel production and is a waste being disposed. The utilization of such seed cake for synthesis of valuable carbon materials is always advantageous over other biomass based precursors in many aspects. Manufacture of value-added products using low-value byproducts of biodiesel production will definitely help in commercialization of biodiesel. Additionally, these plants can be grown once in a lifetime with continuous harvest, providing a potential opportunity for carbon sequestration by afforestation and reforestation [31]. Carbon sequestration by forests has been considered a promising near-term mitigation option for anthropogenic greenhouse gas (GHG) emission [17]. Thus, development of CO_2 adsorbent using aforesaid kind of biomass waste provides potential means of addressing current global challenges, namely energy insecurity and climate change through an integrated approach towards sustainable development.

In the light of these prospects, the current work involves the synthesis and characterization of carbon material, obtained from *Mesua ferrea* L. seed cake, followed by investigation on its CO_2 capture performance. To this end, powdered seed cake was carbonized using hydrothermal treatment and the resulting hydrochar was calcined at different temperatures (425 °C, 500 °C, 575 °C, 650 °C, and 725 °C). The sample, calcined at 650 °C, exhibited maximum CO_2 sorption capacity and hence used for further study. For comparision, another sample was obtained by direct calcination of powdered cake at 650 °C under N_2 atmosphere.

2. Material and methods

2.1. Material synthesis

The starting material (seed cake) was obtained from *Mesua ferrea* L. seeds after lipid extraction with mechanical oil expeller. About 30 g of powdered seed cake was mixed with 100 ml distilled water and stirred for about 30 min at laboratory temperature. The dispersion was transferred into a Teflon-lined sealed autoclave and kept at 200 °C for 24 h. The resulting hydrochar was washed with distilled water and dried in an oven at 120 °C for 3 h. It was then subjected to calcination at 650 °C under pure N_2 atmosphere for 4 h. The sample was denoted as HCM. On the other hand, a known quantity of powdered seed cake was subjected to calcination at 650 °C under pure N_2 atmosphere for 4 h without hydrothermal treatment. The sample was designated as PCM.

2.2. Characterization techniques

The textural parameters of samples were determined by N_2 adsorption/desorption at liquid-nitrogen temperature, using a NOVA 1000 Quanta Chrome high-speed gas sorption analyzer. The specific surface area was calculated from the adsorption isotherm using Brunauer–Emmett–Teller (BET) relation. Total pore volume and average pore diameter were obtained using Bopp-Jancso-Heinzinger (BJH) method from desorption isotherm. The micropore area and micropore volume were calculated by applying the t-plot method of de Boer to the adsorption data. The mesopore volume was calculated by subtracting micropore volume from total volume [32]. The functional groups present in samples were characterized by a Fourier transform infrared ray (FTIR) spectrometer (PerkinElmer FTIR spectrum 2). The samples were dried prior to be mixed with KBr powder, and the spectra were recorded in the range of 400–4000 cm^{-1}, with a resolution of 4 cm^{-1}. The C^{13} NMR spectra were recorded on an ECX400 (Jeol) (S) 400 MHz spectrometer. Powder X-ray diffraction (PXRD) analysis was carried out using D2 PHASER table top X-ray powder diffractometer (Bruker) equipped with Cu Kα radiation source and Ni filter. Raman spectra were measured on a HORIBA Jobin Yvon Raman spectrometer using a semiconductor diode laser at 532 nm as the light source. In order to analyze the surface morphology of samples, scanning electron microscope (SEM) images were obtained using Carl Zeiss, Neon 40 FESEM instrument coupled with an energy dispersive X-ray (EDX) spectroscopy (INCA, Oxford). The samples were further characterized by ultimate and proximate analyses. The elements C, H, N, and S were analyzed in a vario MICRO cube CHNS analyzer. The percentage of oxygen was calculated by mass difference. The moisture, volatile matter and ash content were determined according to ASTM protocols. The fixed carbon content was determined by means of difference. The ultimate and proximate analyses were also performed for pristine mesua. The pH of samples was determined by dispersing 1.0 g of each sample in 100 ml distilled water taken in a beaker. The suspension was heated to 90 °C with stirring for 1 h, followed by cooling to laboratory temperature. The pH was measured using pre-calibrated pH meter (Systronics, μ pH 361).

2.3. CO_2 adsorption measurement

The CO_2 adsorption/desorption experiments were performed at atmospheric pressure with a known quantity of sample (∼2.0 g) using a laboratory scale fixed-bed stainless steel reactor of 10 mm internal diameter and 320 mm length. The bed heights for PCM and HCM were found to be 5.67 cm and 4.97 cm respectively. The reactor, equipped with K type thermocouple, was positioned vertically inside an electric furnace. The pressure at both entrance and exit of the adsorption bed was monitored using two pressure transducers. The pressure drop across the bed was found to be negligible for both samples during the experiment. Prior to adsorption, the sample was pre-treated at 250 °C for 1 h under helium flow (30 ml min^{-1}) and cooled to laboratory temperature (30 °C). A gas mixture of 10% CO_2 balanced by helium was passed through the bed at a flow rate of 20 ml min^{-1}. Then, a portion of column effluent gas was fed to gas chromatograph Mayura, 1100 equipped with a porapak Q column and a thermal conductivity detector. The breakthrough capacity (q_{BT}) and saturation adsorption capacity (q_{SA}) of sample were evaluated using the data of CO_2 concentration at exit, obtained from integrating the gas chromatograph peak area with necessary corrections for blank experiment. After attaining saturation, the sample was flushed with helium at a rate of 30 ml min^{-1} for 1 h and the desorption proceeded at 250 °C. The adsorption and desorption were continued to estimate multicycle stability. The experiment was repeated at least twice for first adsorption capacity to ascertain reproducibility of results.

2.4. Temperature programmed desorption (TPD)

In order to determine the basic site density of samples, the CO_2 TPD was performed using a quartz micro-flow-column system operated at atmospheric pressure. The sample (100 mg) was pretreated under pure helium flow (30 ml min^{-1}) at 200 °C for 30 min. The sample was then cooled to 30 °C and saturated with CO_2 using 10% CO_2/90% He premixed gas for 60 min. After purging the system with helium for 30 min to remove trapped CO_2, the temperature of the system was raised to 650 °C at a ramping rate of 5 °C min^{-1} under a constant flow rate of helium at 30 ml min^{-1}. Thermal conductivity detector (TCD) was used to monitor the effluent CO_2 concentration. For each sample, the blank test was carried out using the same procedure except saturating the sample with CO_2. Prior to the experiment, the TCD response was calibrated by injecting a series of known volumes of the premixed CO_2 gas.