Valorization of coffee grounds to biochar-derived adsorbents for CO_2 adsorption

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ABSTRACT

Global warming is mainly caused by the continuous increase of CO_2 concentration from the enormous utilization of fossil fuels in the environment. To circumvent this problem, it is crucial to develop an efficient and economic method to capture CO_2 from large stationary sources, such as coal-fired power plants, cement, steel factories, and so on. In this study, the CO_2 adsorbents are prepared with biomass wastes (coffee grounds) by combining ammoxidation process (via three different methods) and potassium hydroxide activation. Various spectroscopic and analytical techniques, such as high resolution scanning electron microscope, nitrogen adsorption-desorption isotherms, elemental analysis, Fourier-transformed infrared spectroscopy and X-ray photoelectron spectroscopy are used to study the physicochemical properties of various adsorbents. Carbon dioxide adsorption capacities of prepared adsorbents are measured by using a thermogravimetric analyzer at atmospheric pressure. Furthermore, we test the stability and selectivity of adsorbents by measuring ten CO_2 adsorption-desorption cycles and selectivity of CO_2 and N_2. Results obtained from this study reveal that the adsorbents which are nitrogen-doped by melamine from ammoxidation treatments, followed by potassium hydroxide chemical activation, have highly developed microporosity, high amounts of N-doping and more pyrrolic nitrogen (active adsorption sites), resulting in the highest CO_2 uptake of 2.67 mmol CO_2 $g^{-1}_{sorbent}$ at 35 °C. Most importantly, these biochar-derived adsorbents have excellent selectivity ($[CO_2/N_2]$ = 74.2) for CO_2−N_2 separation and good cyclic stability of CO_2 adsorption-desorption process, which may be suitable for practical applications in capturing CO_2 emitted from coal-fired power plant.

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1. Introduction

Owing to the massive consumption of fossil fuels such as coal, oil and natural gas, the huge emissions of CO_2 which lead to the global warming effect have been a critical issue nowadays (Petrescu et al., 2017). It is important to develop efficient and economical technologies for capturing CO_2 from dominant stationary sources, *e.g.*, coal-burning power plants. Among numerous techniques, the conventional technology in the post-combustion operation, *i.e.* amine absorption, is limited by the high operation costs.

In the recent years, heterogeneous solid adsorbents, for instance, microporous zeolites, porous carbon materials and ordered mesoporous silicas are widely investigated in the field of CO_2 capture. Liu et al. (2011, 2012) reported that the direct incorporation of tetraethylenepentamine (TEPA) onto the as-synthesized

mesoporous silica supports was found to reach a remarkable CO_2 adsorption capacity. Nasri et al. (2014) found that the porous carbons recovered from palm agricultural waste can possess the CO_2 adsorption capacities of 1.66 mmol g^{-1} at 1 bar and 7.32 mmol g^{-1} at 4 bar. Saha et al. (2017) demonstrated that the high surface area of nitrogen-doped porous carbons from lignin was observed to have superior CO_2 capture. Zhang et al. (2017a) proposed that the hydrophobic linear polyethylenimines/silica adsorbents can decrease the water adsorption capacity and retain CO_2 capture. Nevertheless, silica-based adsorbents have difficulties in the poor CO_2 selectivities, stability and tolerance to water moisture in the flue gas, which hinder their practical applications. Among all solid adsorbents, porous carbon adsorbents are promising because of their distinctive properties, *e.g.*, highly chemical and thermal durability, tunable pore architecture and tolerance to water moisture. Su et al. (2009) have found that carbon nanotubes modified with 3-aminopropyl-triethoxysilane can possess surpassing adsorption performance of CO_2 which can be applied as low-temperature adsorbents for CO_2

capture from flue gas. Jimenez et al. (2012) investigated that activated amorphous carbon possessed the superior CO_2 capture capacity of 72.0 wt % of CO_2 at 26 °C and 8 bar among various carbons (carbon nanofibers and amorphous carbon). Wickramaratne and Jaroniec (2013) proposed the synthesis of carbon spheres via carbonization of phenolic resin spheres which can exhibit high CO_2 adsorption capacities of 4.55 mmol g^{-1} at 25 °C. Zhang et al. (2017b) showed a facile one-pot route to prepare hierarchical porous nitrogen-doped carbons which have an excellent CO_2 adsorption capacity of 1.66 mmol g^{-1} at 75 °C and 1.0 bar. However, in terms of the massive production of porous carbon adsorbents, the total costs can be lowered because the adsorbents can be prepared by using biomass as carbon sources which are inexpensive, abundant and sustainable. The United Nation Environment Programme (UNEP) estimated that about 140 billion metric tons of biomass is produced on the earth every year. The recycling of biomass waste (*i.e.* agricultural residues) for the manufacture of carbonaceous adsorbents has received much attention. Recently, many studies have been done by recovering biomass wastes, for example, coconut shells (Yang et al., 2015), weeds (Guzel et al., 2017), nut shells (Kumar et al., 2017), orange peel (Lam et al., 2017), rice husk (Olivares-Marin and Maroto-Valer, 2012), and perennial cane (Singh et al., 2017), as the precursors for the preparation of porous carbons. The CO_2 emissions should be decreased due to the reduced usage of incinerators for these organic wastes. Meanwhile, the recovery of natural resources can be simultaneously achieved from the viewpoint of waste management.

In the present study, the preparation of biochar-derived adsorbents via a simple and low-cost route was proposed. Because different ammoxidation processes would influence the N speciations of active sorption sites and porous architecture on carbons, the coffee grounds were treated by three different ammoxidation methods and then activated by KOH. Among the aforementioned ammoxidation processes, the combination of hydrothermal carbonization with nitrogen-rich precursor (melamine) is an effective approach for synthesizing nitrogen-doped porous carbons. Generally, the hydrothermal carbonization process can be performed at low temperatures (*i.e.*, <200 °C) and moderate pressure, resulting in the formation of versatile morphologies and abundant functional groups. Compared to the conventional pyrolysis route, the hydrothermal carbonization process may preserve high nitrogen content in the resultant carbons. The CO_2 adsorption performance of prepared adsorbents was tested at different temperatures and their cyclic stability and selectivity toward CO_2 adsorption were also investigated. Therefore, the result of this work not only provides the possible route to recover inexpensive biological wastes for the synthesis of high-end biochar-derived adsorbents but also demonstrates the low-cost applications of preventing CO_2 emissions from the power plants.

2. Experimental sections

2.1. Adsorbents preparation

Biochar-derived carbons were prepared from coffee grounds (Nespresso) (Fig. 1a) by preliminarily drying at 100 °C for 12 h to eliminate water moisture. The dried coffee grounds were packed in a quartz reactor, ramped to 400 °C under N_2 flow (100 mL min^{-1}), and maintained at that temperature for 1 h. The carbonized carbon from coffee grounds was denoted as HC (Fig. 1b). Three different methods were proposed to perform the ammoxidation of HC. For the first route (modified by the work of Hou et al. (2010)), ca. 0.2 g of HC was dispersed in 25 mL of absolute alcohol containing 2 mL of 3-Aminopropyltrimethoxysilane (APTES) (99%, Fluorochem). The mixture was refluxed at 80 °C for 24 h, followed by washing

repeatedly with mixture of water and absolute alcohol. After drying at 60 °C overnight, the resulting sample was denoted as SHC. For the second route (modified by the work of Mishra and Ramaprabhu (2012)), ca. 0.2 g of HC was dispersed in 50 mL of HCl. Then, the mixture was further treated with poly-condensation of aniline (5 mL) (95%, Tokyo Kasei Kogyo Co. Ltd) by $K_2Cr_2O_7$ (99%, Sigma-Aldrich) in an ice bath for 6 h. After that, the adsorbent composites were filtered, washed with deionized water and ethanol. Finally, the resultant adsorbents (denoted as PHC) were dried in a vacuum oven at 60 °C. For the third route, 0.5 g of HC was dissolved in 50 mL of H_2O via sonication treatment (Delta, D80H). Afterward, ca. 0.5 g of melamine (99%, Acros) was introduced into the above solution. The resulting mixture was transferred to a Teflon-lined autoclave for further hydrothermal treatments at 160 °C for 24 h. At last, the solution was filtrated and dried at 60 °C in a vacuum oven (DENG YNG, DOV-40) and the obtained solid was denoted as MHC (Fig. 1c). To activate the aforementioned SHC, PHC and MHC, physical mixtures of KOH and prepared samples in the weight ratio of 2:1 were placed in a quartz reactor and then heated to the temperature of 400 °C for 1 h, followed by ramping to 600 °C for another 1 h. The resultant black solids (denoted as KSHC, KPHC and KMHC (Fig. 1d), respectively) were washed several times with 1 M of HCl and d dried under vacuum at 60 °C.

2.2. Characterization methods

The morphologies of the adsorbents were investigated by a field-emission scanning electron microscope (SEM, JEOL JSM-7000F) which were operated at accelerating voltages of 20 kV. N_2 sorption isotherms were collected at −196 °C by using a volumetric technique (Micromeritics ASAP 2020). The Brunauer-Emmett-Teller (BET) specific surface area (S_{BET}) was calculated from nitrogen adsorption data in the relative pressure (P/P_0) range between 0.05 and 0.2. The total pore volume (V_{total}) was estimated from the amount of nitrogen adsorbed at the P/P_0 of 0.99. Fourier transform infrared (FTIR) spectra were recorded on a spectrometer (Bruker, TENSOR 27, 400−4000 cm^{-1}). X-ray photoelectron spectroscopy (XPS) analysis of samples was performed by using a Kratos AXIS Ultra DLD spectrometer system with a monochromatic Al Kα X-ray source (1486 eV). Thermal stability of the prepared adsorbents was tested by a thermogravimetric analyzer (TGA, PerkinElmer Pyris 6) at a heating rate of 10 °C min^{-1} from room temperature to 800 °C under a N_2 flow.

2.3. CO_2 adsorption system

A modified TGA system was used to evaluate the adsorption and desorption performance of prepared adsorbents. Typically, ca. 10 mg of adsorbents were packed in a cell and then heated to 100 °C under N_2 flow (50 mL min^{-1}). Afterwards, the temperature was kept at 100 °C for 30 min in order to guarantee no weight loss, followed by cooling down to 35 and 50 °C for the respective CO_2 adsorption. By introducing high purity of dry CO_2 (99.99%) to the TGA reactor at a flowrate of 50 mL min^{-1}, sorption process was performed for 60 min. After the sorption stage, the gas was changed to pure N_2 (50 mL min^{-1}) to perform desorption process at 75 °C for 30 min. The enthalpies of adsorption were obtained by measuring heat flow of DSC in the TGA system. The ten cycles of sorption/desorption measurements were also investigated to assess the stability of the prepared adsorbents. The sensitivity and accuracy of TGA microbalance are 10 μg and 0.1%, respectively. A relative standard deviation within 5% was found in the repeating TGA tests.