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Activated carbon derived from bio-waste hemp hurd and retted hemp hurd for CO_2 adsorption

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ABSTRACT

Hemp hurd is a bio-waste by-product with unique porous structure. The morphology and thermal properties of original hemp hurd and retted hemp hurd were investigated before the carbonization. Then the biomass carbon materials from hemp hurd and retted hemp hurd were activated by using CO_2 or $ZnCl_2$. The effect of physical activation and chemical activation on the properties of derived carbon was compared. The obtained activated carbons have been evaluated for CO_2 capture. The results indicated that hemp hurd has different porous structure in the cross section and longitudinal section. Retting process can further improve the thermal stability of hemp hurd. The yield, specific surface area, porosity and gas adsorption properties of activated carbons by $ZnCl_2$ activation were superior than those of products from CO_2 activation. By applying $ZnCl_2$ activation, all the activated carbons exhibited significant of micropores with the surface area exceeding 1100 m^2/g. The activated carbon derived from hemp hurd exhibited larger micropore and mesopore volumes than those derived from retted hemp hurd. Enhanced CO_2 adsorption capacity of activated carbons derived from retting process may be attributed to the introduction of surface functionality.

1. Introduction

Hemp grows quickly in most locations and climates with only moderate water and fertilizer requirements and without much need of pesticides [1]. Hemp has been the most important raw material for more than 2000 years as textile fibre, ropes, thread sacks and paper, and has played a significant role in human civilization. In hemp fibre production, hemp hurd, which accounts for about 70–80% of hemp stalk, is regarded as residue by-product [1–5]. Retting is the process of using microbes and moisture on plants to dissolve the cellular tissues and pectins surrounding the bast-fibre bundles to separate the fibres from the stem [1]. Recycling bio-waste hemp hurd and retted hemp hurd to produce useful end products, such as activated carbons for different applications such as gas adsorption and energy storage devices [6,7], would bring significant economic benefit to the industry. Various raw materials such as agricultural and forest biomass, coal, petroleum residues, and bones have been used as activated carbon precursors [8–13]. Compared to those carbon sources, hemp hurd has unique hierarchical pore structures and connected macropores, which are inherently for water and nutrients transportation during the plant growth [3–5], providing an opportunity for preparing activated carbon with low gas diffusion resistance in gas adsorption applications [14–17].

In previous studies, different hemp products have been used as activated carbon precursors [2–5]. Rosas et al. [3] prepared activated carbons by chemical activation of hemp fibres with phosphoric acid at different carbonization temperatures and impregnation ratios. Hemp-derived activated carbon fibres with 1350 m^2/g of apparent surface area and 1.25 cm^3/g of mesopore volume were obtained, and water vapor adsorption was also investigated. Wang et al. [4] synthesized activated carbon nanosheets from hemp bast fibre for ultrafast supercapacitors. An energy density of 8–10 Wh kg^{-1} was achieved at a charge time less than 6 s. Yang et al. [5] prepared activated carbon from hemp stem with KOH activation for gas adsorption. They found that the gas adsorption capacity was dominated by ultramicropores at lower pressure, and then lager micropores and mesopores contributed more at higher pressure. As the results, hemp products can be a suitable candidate to synthesis porous carbon materials, though the main by-product, hemp hurd or retted hemp hurd, has not been systematically studied for activated carbon preparation.

In this study, we investigated the morphology and thermal properties of original hemp hurd and retted hemp hurd, $ZnCl_2$ and CO_2 were used as activation agents. The effects of different activation agents on activated carbon synthesis were investigated. The adsorption isotherms were performed for better understanding the pore formation and the

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derived adsorption properties.

2. Experimental

2.1. Materials and preparation of activated carbon

Original hemp hurd and retted hemp hurd samples were obtained from Ecofibre Industries Operations Pty Ltd, Australia. The hemp hurd and retted hemp hurd was cut and dried in the oven for 12 h at 100 °C before use. All chemicals used in the investigation such as $ZnCl_2$ and HCl were of analytical grade.

Activated carbons produced by CO_2 activation were carried out in a two-step process: (i) The biomass was pyrolyzed in a tubular furnace under the N_2 flow. The temperature was ramped from ambient temperature to 850 °C at a heating rate of 10 °C/min with retention time of 2 h. Then the reactor was cooled down naturally to 800 °C under nitrogen atmosphere. (ii) The reactor was kept 800 °C under the CO_2 flow with retention time of 2 h, then cooled down naturally to the room temperature under CO_2 atmosphere. The obtained activated carbons from hemp hurd and retted hemp hurd are labeled as AC-HH-CO_2 and AC-RH-CO_2.

Activated carbons produced by $ZnCl_2$ activation [18–21] were carried out in three stages: (i) The biomass was impregnated by $ZnCl_2$ solution for 24 h (the weight ratio of $ZnCl_2$ to biomass is 2) then dried at 110 °C for 24 h. (ii) The impregnated biomass was pyrolyzed in a tubular furnace under the nitrogen flow. The temperature was ramped to 800 °C at a heating rate of 10 °C/min with retention time of 2 h. Then the reactor was cooled down naturally to the room temperature. (iii) The obtained samples were washed in 1 mol/L HCl, rinsed by distilled water to neutral PH, and then dried in the oven at 80 °C. The obtained activated carbons from hemp hurd and retted hemp hurd are labeled as AC-HH- $ZnCl_2$ and AC-RH- $ZnCl_2$.

2.2. Characterization

Scanning electron microscope (SEM) images were collected on a Hitachi TM-1000 instrument (HITACHI, Japan) at an accelerating voltage of 15 kV. The thermal properties were characterized using differential scanning calorimetry (DSC) on a TGA/DSC1 analyzer (Mettler-Toledo, Switzerland). The samples were heated to 350 °C at 10 °C/min, and maintained for 3 min to erase thermal history, prior to cooling down to 25 °C at 25 °C/min. A second scan from 25 °C to 350 °C at 10 °C/min was performed. The samples were kept under a nitrogen flow of 20 mL/min throughout the whole process. The melting temperatures (T_m) were determined from the second scan. Sorption isotherms of N_2 at 77 K and CO_2 at 273 K were measured with a TriStar II 3020 apparatus (Micromeritics, USA) after degassing the activated carbon at 473 K and a pressure of 10^{-5} Torr for 24 h. The N_2 isotherms were used to determine the Brunauer Emmett Teller (BET) specific surface area and Langmuir specific surface area; total pore volumes; micropore volumes using the t-plot method and mesopore volumes from the Barrett Joyner Halenda (BJH) method. The activated carbons were degassed at 423 K for 24 h prior to high pressure adsorption measurements.

3. Results and discussion

The SEM images of raw hemp materials and activated carbons are shown in Fig. 1, in which Fig. 1(a,b) are the full view of hemp hurd of different angles, (c,d) are the longitudinal and cross section of hemp hurd, (e,f) are the longitudinal and cross section of retted hemp hurd, and (g,h) are the obtained activated carbons AC-HH-CO_2 and AC-HH-$ZnCl_2$. Fig. 1(a,b) shows that hemp hurd has a unique structure which consists of two types of macropore channels of different sizes. One type is the round like or elliptic large pore channels with 40–60 μm in diameter, which is resulted from the vascular bundles. Another type of pore channel is the polygonal or round like pores with smaller diameter, 20–30 μm, which derives from the ground tissues and continuously distribute like honeycomb around the large pores [1,3,5]. The channels are parallel to the growth direction of the hemp hurd result from water and nutrients transportation. These pore channels also have high porosity on its inner wall, leading to the formation of hierarchical pore structures and connected pore geometry. Retting process corroded part of the larger pore channels and turned some of them into a coil like structure (Fig. 1(e,f)). The thermal stability of hemp hurd is improved by retting (Supplementary Section, Fig. S1), showing the increase of decomposition temperature. From Fig. 1(g,h), the activated carbons by both CO_2 activation and $ZnCl_2$ activation retain the original connected pore geometry of hemp hurd.

Table 1 summarizes the yield, specific surface area pore and pore volume of the obtained activated carbons. During CO_2 activation, porosity is developed by carbon gasification at high temperature due to the reaction "$C + CO_{2-} > 2CO$". CO_2 reacts with the carbon in hemp hurd at high temperatures. This process of gasification develops porosity and high surface area [22]. During $ZnCl_2$ activation, $ZnCl_2$ act as templates for the pore formation. Firstly, $ZnCl_2$ can act as a dehydrating agent, catalyzing the scission of glycosidic bonds and the elimination of hydroxyl and carbonyl groups in hemp hurd during the heating. Secondly, the fused $ZnCl_2$ can react with H_2O generated from the cleavage of the biopolymer in hemp hurd, leading to the formation of $Zn_2OCl_2{\cdot}2H_2O$. Then, $ZnCl_2$ gas can be generated from the decomposition of $Zn_2OCl_2{\cdot}2H_2O$, and the gas diffusion developed pathways through the thermoplastic phase, creating the pore structure and high surface area of the obtained activated carbon [23].

The yields of the activated carbons by $ZnCl_2$ activation reached 30% while those by CO_2 activation are about 20%. This is because some CO_2 reacted with the samples during the pyrolysis but there is no sample consumption in N_2 atmosphere by $ZnCl_2$ activation. $ZnCl_2$ activation also provides higher surface areas and pore volume of the activated carbons than CO_2 activation. The BET surface areas of the activated carbons by $ZnCl_2$ activation are greater than 1100 m^2/g. The $ZnCl_2$ activation provides significant contributions of micropores to the total surface area. Rosas et al. [2] showed that the surface area of activated carbon derived from hemp fibre reached 1355 m^2/g in their best experimental parameter. In our study, the activated carbon derived from bio-waste original retted hemp hurd had the highest BET surface area of 1431 m^2/g, which can be considered as a competitive precursor of activated carbons.

Fig. 2 shows the adsorption and desorption of N_2 at 77 K on activated carbons. From Fig. 2 we can see that the activated carbons by $ZnCl_2$ activation exhibited Type I isotherms. The significant adsorption of N_2 at $P < 10$ kPa is attributed to the adsorption in the micropores derived by $ZnCl_2$ activation. The adsorption isotherms of the AC-HH-CO_2 exhibited type I behavior while AC-RH-CO_2 exhibited type IV behavior. Type IV isotherms describe adsorption in AC-RH-CO_2 with a mixture of micropores and mesopores. Table 1 also confirms that the mesopores volume of AC-RH-CO_2 is dominant and also higher than that of other activated carbons.

Fig. 3 shows the adsorption of CO_2 at 273 K on activated carbon prepared from hemp hurd and retted hemp hurd by CO_2 activation and $ZnCl_2$ activation. The CO_2 adsorption capacities of activated carbons from $ZnCl_2$ activation are higher than those by CO_2 activation, which is related to their higher surface areas and pore volume. AC-RH-$ZnCl_2$ had the highest CO_2 adsorption capacities. This may related to their high surface functionality and morphological differences which needs further exploration.

4. Conclusions

Hemp hurd and retted hemp hurd have been used as the precursors to prepare activated carbon by $ZnCl_2$ activation and CO_2 activation. The obtained activated carbons retained the original hierarchical pore structures and connected macropores of hemp hurd. $ZnCl_2$ activation