

HEMP HURD DERIVED ACTIVATED CARBON FOR CO₂ ADSORPTION

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ABSTRACT

Hemp hurd were used to prepare activated carbon with high surface area. The effect of CO₂ activation and ZnCl₂ activation on the properties of derived carbon was compared. The effect of ZnCl₂ impregnation rate on the properties of activated carbon was also studied. The obtained activated carbons have been evaluated for CO₂ capture. The results indicated that hemp hurd and retted hemp hurd have unique porous structure. The obtained activated carbons retained their porous structure. The activated carbon derived from hemp hurd exhibited better CO₂ adsorption capacity, and larger micropore and mesopore volumes than those derived from retted hemp hurd. The yield, specific surface area, porosity and gas adsorption properties of activated carbons by ZnCl₂ activation were superior than those of products from CO₂ activation. The yield, specific surface area, porosity and gas adsorption properties of activated carbons by ZnCl₂ activation increased with the increase of ZnCl₂ impregnation rate.

1 INTRODUCTION

In hemp fibre production, hemp hurd, which accounts for about 70-80% of hemp stalk, is regarded as residue by-product [1]. Recycling bio-waste hemp hurd to produce useful end products would bring significant economic benefit to the industry [1-3]. Various raw materials such as agricultural and forest biomass, coal, petroleum residues, and bones have been used as activated carbon precursors [4-10]. Compared to those carbon sources, hemp hurd has unique hierarchical pore structures and connected macropores, providing an opportunity for preparing activated carbon with low gas diffusion resistance in gas adsorption applications [1-3].

In previous studies, activated carbons were prepared by chemical activation of hemp fibres with phosphoric acid at different carbonization temperatures and impregnation ratios [2]. Hemp-derived activated carbon fibres with 1350 m²/g of apparent surface area and 1.25 cm³/g of mesopore volume were obtained, and water vapor adsorption was also investigated. Activated carbon from hemp stem with KOH activation for gas adsorption was prepared [3]. The gas adsorption capacity was dominated by ultramicropores at lower pressure, and then larger micropores and mesopores contributed more at higher pressure. In this study, we investigated the morphologies of original hemp hurd and retted hemp hurd, ZnCl₂ and CO₂ were used as activation agents. The effects of ZnCl₂ activation and CO₂ activation on activated carbon synthesis were investigated. The effect of ZnCl₂ impregnation rate on the properties of activated carbon was also studied. The adsorption isotherms were performed for better understanding the pore formation and the derived adsorption properties.

2 EXPERIMENTAL

2.1 MATERIALS AND ACTIVATED CARBON PREPARATION

Hemp hurd and retted hemp hurd samples were obtained from Ecofibre Industries Operations Pty Ltd, Australia.

Two-step process was used to obtain activated carbons by CO₂ activation: (i) The biomass was pyrolyzed in a tubular furnace under the N₂ flow at 850 °C at a heating rate of 10 °C/min with retention time of 2 h. Then the reactor was cooled down to 800 °C. (ii) The reactor was kept 800 °C under the CO₂ flow with retention time of 2 h, then cooled down naturally to the room temperature. The obtained activated carbons from hemp hurd and retted hemp hurd are labelled as AC-HH-CO₂ and AC-RH-CO₂.

Three-step process was used to obtain activated carbons by ZnCl₂ activation: (i) The biomass was impregnated by ZnCl₂ solution for 24 h (the weight ratio of ZnCl₂ 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 at the carbonization temperature of 800 °C are labelled as AC-HH- ZnCl₂ and AC-RH- ZnCl₂. Another group of activated carbons from retted hemp hurd by ZnCl₂ activation on 500 °C at different impregnation rates (2:1, 3:1, 4:1) are labelled as AC-ZnCl₂-2:1, AC-ZnCl₂-3:1, AC-ZnCl₂-4:1.

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. Sorption isotherms of N₂ at 77 K and CO₂ 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 N₂ 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) is the full view of hemp hurd, (b) is the internal pore structure of hemp hurd, (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-CO₂ and AC-HH-ZnCl₂. Fig. 1(a,b) shows that hemp hurd has a unique structure which consists of two types of macropore channels. 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)). From Fig. 1(g,h), the activated carbons by both CO₂ activation and ZnCl₂ activation retain the original connected pore geometry of hemp hurd.

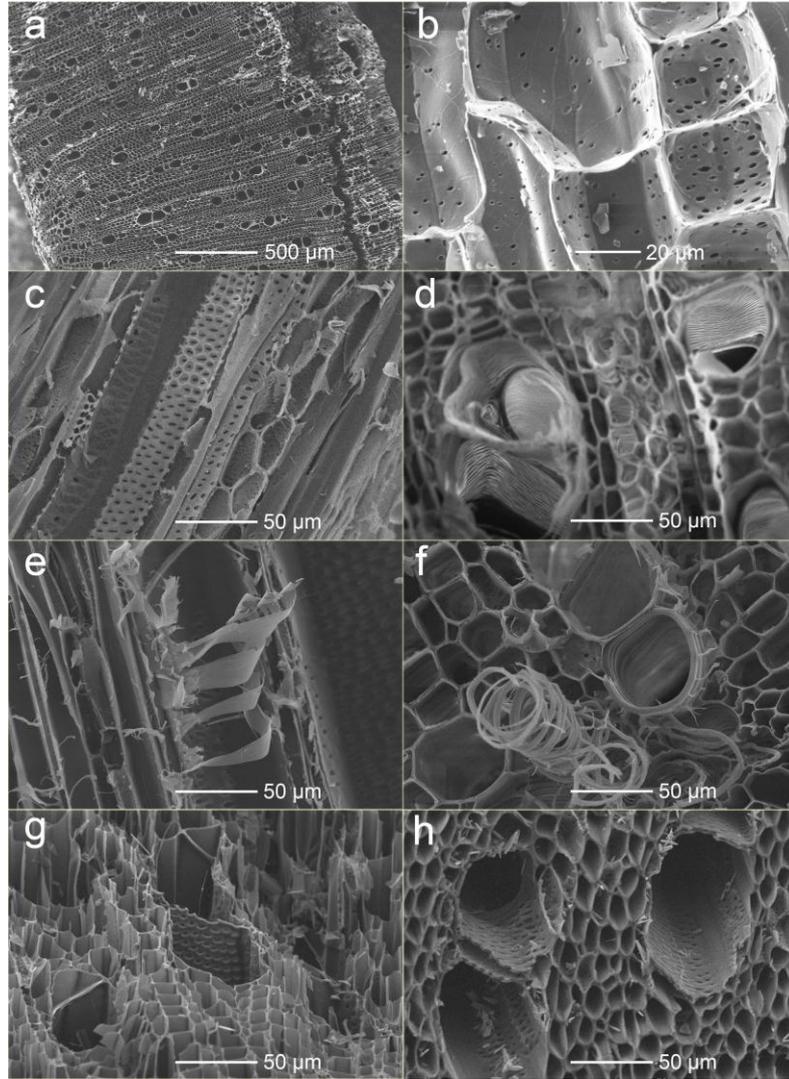


Figure 1: SEM pictures of (a) full view of hemp hurd, (b) the internal pore structure of hemp hurd, (c,d) the longitudinal and cross section of hemp hurd and (e,f) the longitudinal and cross section of retted hemp hurd and (g,h) the AC-HH-CO₂ and AC-HH-ZnCl₂.

Sample	Yield	N ₂ adsorption				
		S _{BET} (m ² ·g ⁻¹)	S _{Langmuir} (m ² ·g ⁻¹)	V _{total} (cm ³ ·g ⁻¹)	V _{micro} (cm ³ ·g ⁻¹)	V _{meso} (cm ³ ·g ⁻¹)
AC-HH-CO ₂	20.7%	489	545	0.198	0.170	0.008
AC-RH-CO ₂	20.2%	632	783	0.347	0.174	0.108
AC-HH-ZnCl ₂	30.3%	1431	1669	0.583	0.467	0.006
AC-RH-ZnCl ₂	28.6%	1128	1259	0.442	0.393	0.002

Table 1: Yield, specific surface area and pore volume of the activated carbons obtained from N₂ isotherms at 77 K.

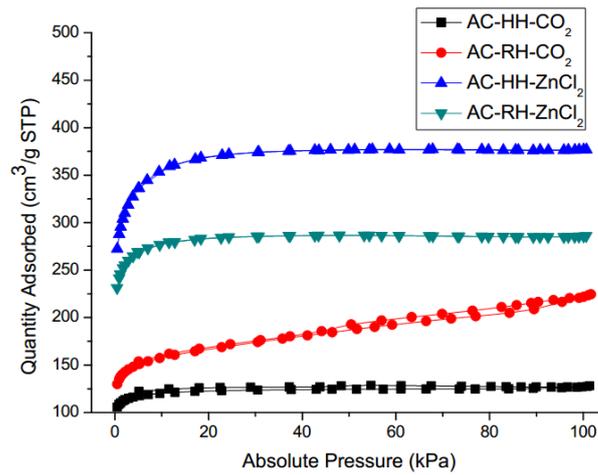


Figure 2: Measurements of specific surface area and pore volume of the activated carbons by CO₂ activation and ZnCl₂ activation.

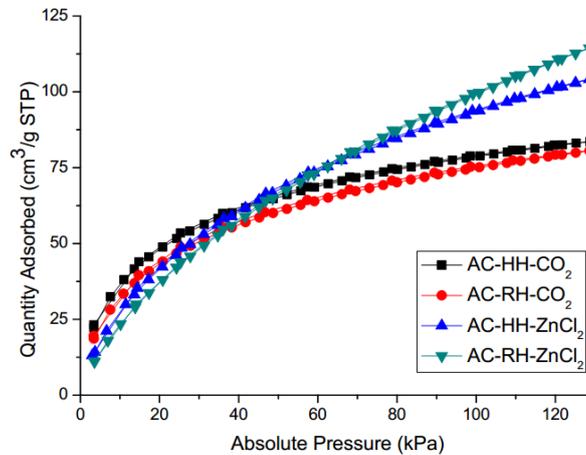


Figure 3: Adsorption of CO₂ at 273 K on activated carbons by CO₂ activation and ZnCl₂ activation.

Fig. 2 shows the adsorption and desorption of N₂ at 77 K on activated carbons by CO₂ activation and ZnCl₂ activation. Table 1 summarizes the yield, specific surface area pore and pore volume of the obtained activated carbons. Activated carbons by ZnCl₂ activation exhibited Type I isotherms. The significant adsorption of N₂ at P<10kPa is attributed to the adsorption in the micropores derived by ZnCl₂ activation. The adsorption isotherms of the AC-HH-CO₂ exhibited type I behavior while AC-RH-CO₂ exhibited type IV behavior. Type IV isotherms describe adsorption in AC-RH-CO₂ with a mixture of micropores and mesopores. The yields of the activated carbons by ZnCl₂ activation reached 30% while those by CO₂ activation are about 20%. This is because some CO₂ reacted with the samples during the pyrolysis but there is no sample consumption in N₂ atmosphere by ZnCl₂ activation. ZnCl₂ activation also provides higher surface areas and pore volume of the activated carbons than CO₂ activation. The BET surface areas of the activated carbons by ZnCl₂ activation are greater than 1100 m²/g. The ZnCl₂ activation provides significant contributions of micropores to the total surface area.

Fig. 3 shows the adsorption of CO₂ at 273 K on activated carbon prepared from hemp hurd and retted hemp hurd by CO₂ activation and ZnCl₂ activation. The CO₂ adsorption capacities of activated carbons from ZnCl₂ activation are higher than those by CO₂ activation, which is related to their higher

surface areas and pore volume. AC-RH-ZnCl₂ had the highest CO₂ adsorption capacities. This may related to their high surface functionality and morphological differences. Then activated carbons derived from retted hemp hurd by ZnCl₂ activation at different impregnation rate were investigated.

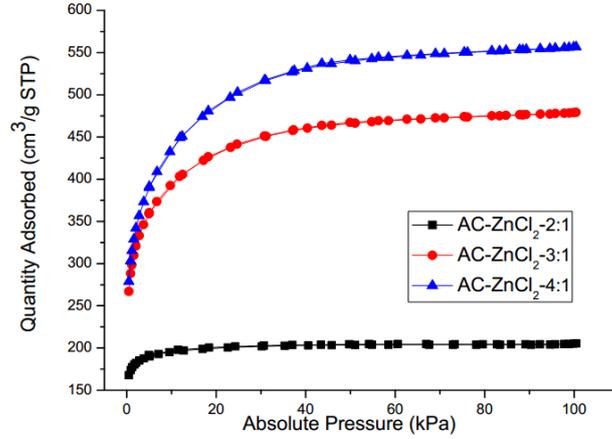


Figure 4: Measurements of specific surface area and pore volume of the activated carbons from retted hemp hurd by ZnCl₂ activation with different impregnation rate.

Sample	Yield	N ₂ adsorption				
		S _{BET} (m ² ·g ⁻¹)	S _{Langmuir} (m ² ·g ⁻¹)	V _{total} (cm ³ ·g ⁻¹)	V _{micro} (cm ³ ·g ⁻¹)	V _{meso} (cm ³ ·g ⁻¹)
AC-ZnCl ₂ -2:1	54.3%	794	891	0.318	0.273	0.007
AC-ZnCl ₂ -3:1	64.4%	1558	2071	0.741	0.330	0.060
AC-ZnCl ₂ -4:1	64.0%	1708	2411	0.861	0.278	0.084

Table 2: Yield, specific surface area and pore volume of the activated carbons from retted hemp hurd by ZnCl₂ activation with different impregnation rate.

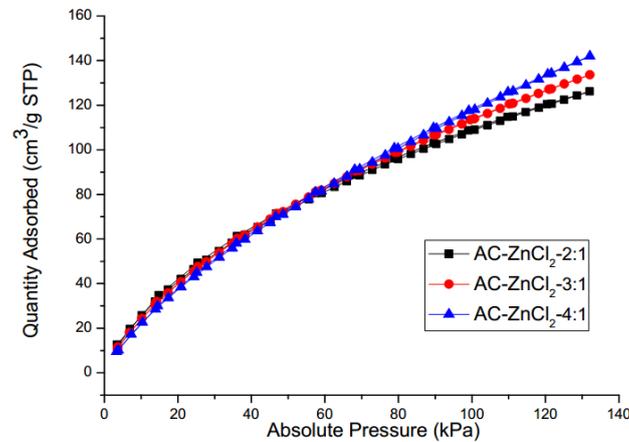


Figure 5: Adsorption of CO₂ at 273 K on activated carbons from retted hemp hurd by ZnCl₂ activation with different impregnation rate.

Fig. 4 shows the adsorption and desorption of N₂ at 77 K on activated carbons prepared from retted hemp hurd by ZnCl₂ activation with different impregnation rate. Table 2 summarizes the yield, specific surface area pore and pore volume of the obtained activated carbons. Activated carbons by ZnCl₂ activation exhibited Type I isotherms. The yields of the activated carbons were more than 50% when the carbonization temperature was 500 °C. The yield, specific surface area and total pore volume of the activated carbons increased with the increase of impregnation rate. The BET surface areas of the activated carbons reached 1708 m²/g when the impregnation rate was 4:1.

Fig. 5 shows the adsorption of CO₂ at 273 K on activated carbon prepared from retted hemp hurd by ZnCl₂ activation with different impregnation rate. The CO₂ adsorption capacities of activated carbons increased with the increase of impregnation rate, which is related to their higher surface areas and pore volume.

4 CONCLUSIONS

Hemp hurd and retted hemp hurd have been used as the precursors to prepare activated carbon by ZnCl₂ activation and CO₂ activation. The obtained activated carbons retained the original hierarchical pore structures of hemp hurd. Retting process corroded part of the larger pore channels of hemp hurd. Retting process may also introduce the surface functionality of hemp hurd which enhanced its CO₂ adsorption capacity. ZnCl₂ activation was more efficient to create micropores in hemp hurd and retted hemp hurd. It also contributes to larger yield, specific surface area, and higher CO₂ adsorption capacities. The yield, specific surface area, porosity and gas adsorption properties of activated carbons by ZnCl₂ activation increased with the increase of ZnCl₂ impregnation rate.

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