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Effects of activation agents and intrinsic minerals on pore development in activated carbons derived from a Canadian peat

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ABSTRACT

Activated carbons (ACs) with very high specific surface areas up to approximately 900 m^2/g and total pore volume up to 0.5 cm^3/g were produced from a Canadian peat through chemical activation using either H_3PO_4 or $ZnCl_2$ as the activation agent, followed by activation/carbonization in air at 450 °C for 45 min. $ZnCl_2$ was found to be more effective for developing microporous structures in the ACs, while H_3PO_4 is more efficient in developing the mesopores. Demineralization of the AC precursor to remove intrinsic minerals greatly affected the development of pore structures during the activation process. The AC derived from the demineralized peat activated by $ZnCl_2$ attained the highest BET surface area with significantly increased micro-/mesopores.

1. Introduction

Activated carbons (ACs) have been widely used as adsorbents or catalytic supports owing to their high surface areas (up to 3000 m^2/g) and porosity (as high as 0.6 cm^3/g) [1–3]. Depending on the types of application, there are different requirements on the pore structures of ACs. For example, in liquid-phase applications, a higher pore volume in the macropore (>50 nm) range is required to prevent liquids from diffusing into the mesopore (2–50 nm) and micropore (<2 nm) regions, whereas in gas-phase applications, a higher pore volume in the meso- and micro-pore region is more desirable [2]. ACs can be produced from a variety of carbonaceous material such as wood, coal, and petroleum-coke through physical/chemical activation [3]. Different activation methods could produce ACs products with different characteristics [4,5]. H_3PO_4 and $ZnCl_2$ have been commonly used as activation agents for ACs production from lignocellulosic materials such as peanut hull, coconut shell, sugar cane bagasse and wood sawdust [5,6].

Peatlands cover an estimated 400 million hectares (about 3%) of the Earth's land surface and Canada contains some 40% of the world's peatlands — about 170 million hectares [7], hence peat can be an immense resource for the production of both fuel and carbon materials. The main objective of this study was to produce and characterize inexpensive ACs from a Canadian peat by chemical activation using H_3PO_4 and $ZnCl_2$, and to examine the effects of activation agent and intrinsic minerals in the raw peat on pore development in the final AC products.

2. Materials and methods

2.1. Peat

The peat sample used, supplied by Peat Resources Ltd, was first dried for 24 h at 105 °C, and then ground with a Wiley mill into particles smaller than 40 mesh. The proximate and elemental (ultimate) analyses of the raw peat are: 65.6 wt.% (db, on a dry basis) volatile matter, 19.0 wt.%(db) fixed carbon, and 5.4 wt.% (db) ash; 54.7 wt.% (daf, dry-and-ash-free) C, 5.5 wt.% H, 2.1 wt.% N, 0.2 wt.% S and 37.5 wt.% O.

In order to determine the effects of the intrinsic minerals of the AC precursor, the peat was demineralized with HCl pretreatment prior to the activation using an 18% HCl solution at 60 °C for 16 h under magnetic stirring in a water bath. After the HCl pretreatment, the peat slurry was filtrated, and the recovered sample was washed with distilled water thoroughly to pH of 6.5–7.0. The demineralization operation markedly reduced the mineral concentrations, particularly the elements of Na, K, Mg, Ca and Fe. The ICP-AES measurements revealed that the contents of these mineral elements in the ash of the demineralized peat were all <0.1 wt.%, while the raw peat ash contains 0.1 wt.% Na, 0.4 wt.% K, 2.3 wt.% Mg, 15.6 wt.% Ca and 11.1 wt.% Fe.

2.2. Production of ACs using H_3PO_4/$ZnCl_2$

According to some previous studies from the literature on activated carbon production by H_3PO_4 and $ZnCl_2$ activation, the optimal activation conditions were: the weight ratio of the activation

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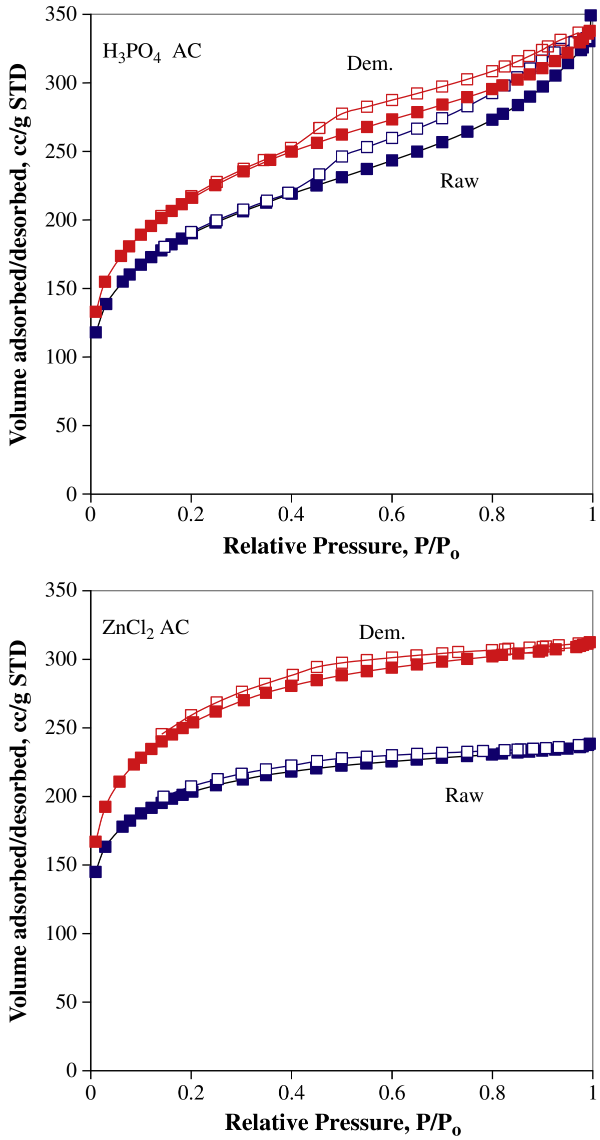

Fig. 1. N_2 adsorption/desorption isotherms of the ACs derived from raw/demineralized peat samples using the activation agent of H_3PO_4 (the upper figure) or $ZnCl_2$ (the bottom figure): The solid and open square symbols represent adsorption and desorption, respectively.

agent to precursor of 1–2, activation/carbonization temperature of 400–500°C and activation time of 0.5–2 h [6,8,9]. Although activation/carbonization of impregnated samples are more commonly carried out under an inert atmosphere, it was found that activation/carbonization of the H_3PO_4 impregnated samples in air or the oxygen derived from the gas phase during the activation process could contribute to the building of the porous structure [6,8]. As the main objective of this study was to investigate the effects of activation agents (H_3PO_4 and $ZnCl_2$) and intrinsic minerals in the raw peat on pore development in the final AC products, the ACs were prepared using the same procedures and under the same activation conditions selected based on the optimal activation conditions as described previously. Specifically, 40 g of the dried raw (or demineralized) peat powder was impregnated with 100 ml of 60 wt.% H_3PO_4 or $ZnCl_2$ at room temperature for 12 h. The sample (loaded in a ceramic crucible) was then thermally activated at 200 °C for 15 min followed by carbonization at 450 °C for 45 min in air. After the sample was cooled down to room temperature, it was washed with distilled water thoroughly to a neutral pH, followed by drying overnight at 105 °C in air. The yields of the resulting ACs, calculated by the weight loss during the carbonization, were 55–60% and 60–62% for the activation with H_3PO_4 and $ZnCl_2$, respectively. The obtained AC samples were designated as H_3PO_4 AC-raw, $ZnCl_2$ AC-raw, H_3PO_4 AC-dem and $ZnCl_2$ AC-dem, wherein the “dem” designates the “demineralized peat”.

2.3. Characterization of the ACs

The obtained AC samples after being outgassed for 2 h at 200 °C were analyzed by N_2 isothermal adsorption (77 K) for its surface area and textural structures on NOVA 1200e/TO from Quantachrome. The Brunauer–Emmett–Teller (BET) method was used to determine the surface area of the samples, and the Barrett, Joyner and Halenda (BJH) method for the pore volumes and structures.

3. Results and discussion

Fig. 1 shows the N_2 adsorption/desorption isotherms of the ACs derived from the raw/demineralized peat samples using different activation agents (H_3PO_4 and $ZnCl_2$). The ACs derived from the demineralized peat consistently show a slightly higher N_2 adsorption capacity than those from the raw peat, suggesting greater surface area and porosity in the ACs from the demineralized precursor.

As shown in the upper figure, H_3PO_4 ACs show isotherms similar to a type between types I, II and/or IV, indicating the presence of both micro-/mesopores. The isotherms for the H_3PO_4 ACs from both raw and demineralized precursors show a hysteresis loop between types of H_3 and H_4, indicative of slit-shaped pores and microporosity [10]. As displayed in the bottom figure, the isotherms of the $ZnCl_2$ AC-raw and $ZnCl_2$ AC-dem samples differ from those for the H_3PO_4 ACs as discussed previously. The isotherms for the $ZnCl_2$ ACs are typical of type II isotherm and H4 hysteresis loop, suggesting that the obtained $ZnCl_2$ ACs are typical microporous materials.

Multi-point BET surface areas, BJH desorption surface areas, total pore volumes, BJH desorption pore volumes, and average pore diameters for all the ACs are presented in Table 1. $ZnCl_2$ is more effective than H_3PO_4 in producing ACs of a higher BET surface area from either the raw or demineralized precursor, but leading to a smaller total pore volume. The BJH desorption surface areas (mainly for mesopore area), the BJH desorption mesopore volumes and the average pore diameters are all greater in the H_3PO_4 ACs than those in the $ZnCl_2$ ACs. The previously mentioned difference in the BET surface areas and pore structures between the H_3PO_4 AC_S and $ZnCl_2$ AC_S suggests different performances of these activation agents in developing pore structures in the ACs. The different performances of

Table 1
Surface areas and textural properties of the peat-derived ACs.

AC precursor	Activation agent	BET[a] (m^2/g)	BJH cumulative desorption surface area (m^2/g)	Total pore volume[b] (cm^3/g)	BJH cumulative desorption pore volume (cm^3/g)	Average pore size (nm)
Raw peat	$ZnCl_2$	700	180	0.36	0.13	2.08
	H_3PO_4	680	380	0.50	0.42	2.97
Demineralized peat	$ZnCl_2$	890	340	0.48	0.24	2.16
	H_3PO_4	770	430	0.51	0.38	2.66

[a] Multi-point BET.
[b] Total pore volume (less than 163 nm).