Short communication

Porous structure and adsorptive properties of hide waste activated carbons prepared via potassium silicate activation

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ABSTRACT

A novel activating agent, potassium silicate, was employed in the preparation of hide waste activated carbon. Effects of different activation temperatures and impregnation ratios on porous activated carbon evolution were evaluated by nitrogen adsorption/desorption. The BET specific surface area and pore volume of prepared activated carbon could attain 2046.12 m^2/g and 1.068 cm^3/g, when the process of preparation carried out at the best conditions (activation temperature of 700 °C and the impregnation ratio of 2:1). Methylene blue (MB) was selected as the adsorbate to evaluate its adsorption property. Adsorption results can be fitted well by the Langmuir isotherm, indicating the maximum monolayer adsorption capacity of MB reached to 769.23 mg/g.

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1. Introduction

Activated carbon, the most common and effective adsorbent, has large specific surface area, complex aperture structure and variety of functional groups, which can be prepared by any carbonaceous materials. Today, waste materials such as macadamia nut endocarp [1], lotus stalk [2], waste tires [3] etc. are transformed into activated carbons, which has become one of the research focuses. When raw hide and skin convert into leather, solid and liquid wastes would produce. The solid waste such as hide waste (HW) had keratin ingredient which was often discarded due to the low economic benefits, thus the reasonable application of this solid waste should be studied further. Nevertheless, according to the literature, there is little information about the preparation of activated carbon from HW.

There are two main activation methods in the preparation of activated carbon, namely physical and chemical methods. As to chemical method, KOH, NaOH, H$_3$PO$_4$ and ZnCl$_2$ were often used as the activating agents [4]. The carbon produced by KOH or NaOH generally has microporous structure, whereas KOH or NaOH can corrode apparatus whose life would be shortened and thus limit

the development and application of this activating agent. Actually, silicone material is widely used as flame retardants in the field of extinguishing as a result of hindering the combustion of materials from originating [5]. However, to our knowledge, there are no papers using potassium silicate (K$_2$SiO$_3$) as the activating agent for preparing activated carbon. The purpose of this study was to prepare hide waste activated carbon (HWAC), using K$_2$SiO$_3$ as the activating agents to evaluate the pore structure and adsorption properties.

2. Materials and methods

2.1. Preparation of activated carbons

HW was provided by a tanning industry from Shandong province in China. The raw material was first soaked with ethanol for 48 h to remove some fat, then washed and dried at 60 °C. The dried materials were cut into particles of 0.5 cm × 0.5 cm, then dipped with a certain concentration of K$_2$SiO$_3$ solution to a varying impregnation ratio of 1:1–3:1 (R, g K$_2$SiO$_3$/g HW). After impregnation for 12 h, the mixtures were heated at 105 °C for 30 min to evaporate some water. Samples were heated to the desired temperatures (400, 500, 600, 700, and 800 °C) in a tube furnace, and maintained for 1 h under a stable nitrogen flow (100 mL/min). The products were washed with hot water and distil water to ensure

the pH of washing liquid attained neutral, and then dried at 105 °C for 12 h. Finally, the desired carbons were sieved to a particle size of 0.076–0.15 nm, and stored in a desiccator for the next study.

2.2. Characterization of HW-K₂SiO₃ and HWAC

The thermogravimetric analysis (TGA) and derivative thermo-gravimetric (DTG) curves of HW after K_2SiO_3 impregnated were acquired by an SDT-simultaneous TGA–DTA model, which were performed in pure N_2 atmosphere (100 mL/min). The mixture was heated at the heating rate of 10 °C from room temperature to 700 °C, and held this temperature for 1 h. The BET specific surface area (S_{BET}) and pore size distribution of HWACs were character-ized using a surface area analyzer (JW-BK122W, China) by N_2 adsorption–desorption isotherm at 77 K. The surface morphology of activated carbon was determined by scanning electron microscopy (SEM) (HitachiS-520, Japan).

2.3. Equilibrium adsorption experiment

Activated carbon under the conditions of the activated tem-perature of 700 °C and the impregnation ratio of 2:1 with the highest S_{BET} (AC) was selected to perform the adsorption experi-ments. Batch experiments were conducted in a series of 150-mL conical flasks containing 50 mL MB and 0.05 g adsorbents with dif-ferent initial concentrations ranging from 75 to 900 mg/L. The flakes were placed in a thermostatic shaker (SHA-B, Shanghai, China) and shaken at 25 °C with a speed of 160 rpm for 24 h to ensure the equilibrium. Finally, the concentrations of MB solution after fil-trating were determined by a UV–vis spectrophotometer (UV-754, Shanghai) at λ_{max} = 665 nm. Blank experiments without adsorbents were also performed as described above. The adsorption isotherm experiments were carried out in duplicate and the mean value was reported. The adsorption capacity, q_e (mg/g), could be calculated by the equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where C_0 and C_e (mg/L) are the initial and equilibrium concentra-tions of MB solutions. V (L) is the solution volume of MB solutions. W (g) is the mass of activated carbon.

2.4. Equilibrium modeling

The equilibrium data of MB adsorption were modeled using Langmuir [6] and Freundlich [7] equations as follows:

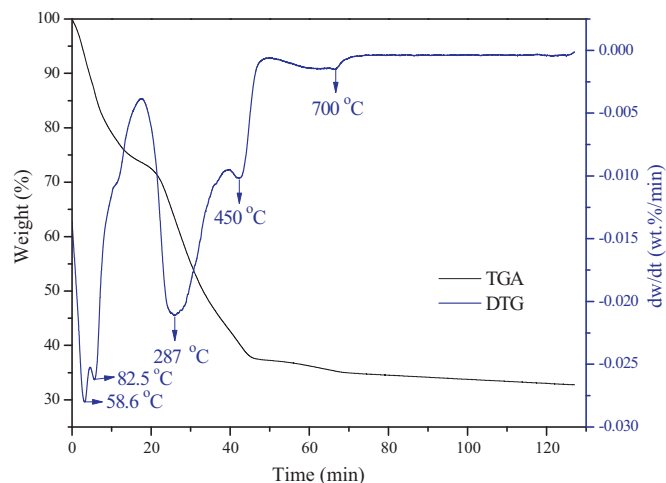$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{2}$$

Fig. 1. TGA and DTG curves for the pyrolysis of HW-K₂SiO₃.

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{3}$$

where q_m and q_e (mg/g) are the maximum and the equilibrium adsorption capacities, respectively. K_L (L/mg) is the Langmuir con-stant related to the free energy of adsorption. K_F (mg/g) (L/mg)$^{1/n}$ and n are the Freundlich constants associated with adsorption intensity.

3. Results and discussion

3.1. Characterization of HW-K₂SiO₃ and HWAC

3.1.1. Thermogravimetric analysis of HW-K₂SiO₃

The TGA and DTG curves of HW-K₂SiO₃ are shown in Fig. 1. TGA profile shows that the process of weight loss contained three sec-tions. The weight loss in the first 20 min could be due to the water evaporation and the degeneration of keratin, reflected in the DTG curve two small peaks. The second stage occurred between 20 min and 45 min, which attributed to the volatile of organic matter and moisture. The peaks at the temperatures of 287 °C and 450 °C in the DTG curve were corresponded with the thermal decomposition of denatured proteins under the catalysis of silicate. After 40 min, the weight loss decreased slightly, illustrating that the catalytic action of K₂SiO₃ completed.

3.1.2. Nitrogen adsorption behavior and porosity development

The N₂ adsorption/desorption isotherms and pore size distribu-tions of the prepared activated carbons under different conditions

Table 1
The effect of activation temperature and impregnation ratio on BET surface areas, pore volumes, average pore sizes of activated carbons activated by K₂SiO₃.

Activated temperature (°C)	R	S_{BET}[a]	S_{mic}[b] (m²/g)	S_{mic}/S_{BET}	V_{tot}[c] (cm³/g)	V_{mic}[d] (cm³/g)	V_{mic}/V_{tot} (%)	D_p[e] (nm)
400		7.93	0.318	4.01	0.071	0.0025	3.52	35.89
500		791.64	697.21	88.07	0.436	0.3371	77.32	2.20
600	2:1	1071.84	1031.29	96.23	0.563	0.4574	81.24	2.10
700		2046.12	1803.20	88.13	1.068	0.8103	75.87	2.09
800		175.05	11.22	6.41	0.567	0.0307	5.41	12.95
	1:1	716.69	616.38	86.00	0.585	0.2961	50.62	3.27
700	1.5:1	1245.70	1115.70	89.56	0.653	0.5054	77.40	2.10
	2.5:1	594.51	495.09	83.28	0.399	0.2435	61.03	2.69
	3:1	333.34	91.87	27.56	0.644	0.1301	20.20	7.72

[a] S_{BET}: BET specific surface area.
[b] S_{mic}: micropore specific surface area.
[c] V_{tot}: total pore volume.
[d] V_{mic}: micropore volume.
[e] D_p: the mean pore.