Journal of the Taiwan Institute of Chemical Engineers 45 (2014) 2801–2804

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Short communication

Activated carbons with well-developed microporosity prepared from *Phragmites australis* by potassium silicate activation

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ARTICLE INFO

Article history:
Received 6 May 2014
Received in revised form 17 July 2014
Accepted 23 July 2014
Available online 26 August 2014

Keywords:
Activated carbon
Microporous
Potassium silicate activation
Preparation
Characterization

ABSTRACT

Potassium silicate (K_2SiO_3) was employed as new activating agent for preparing activated carbons with well-developed microporous structure from a renewable source (*Phragmites australis*, PA). The effects of chemical impregnation ratio (mass of K_2SiO_3: PA, 1.0–2.5) and activation temperature (450–800 °C) on the properties of activated carbons were investigated. Porous textures and surface morphologies of the carbons were characterized by N_2 adsorption/desorption and scanning electron microscopy (SEM). The activation was simulated by thermo-gravimetric analysis. In general, under the experimental conditions investigated, the highest surface area (721 m^2/g) of activated carbons reached at activation temperature of 600 °C and impregnation ratio of 1.5. The produced carbons were mainly microporous and the majority of pore widths of the carbons were below 4 nm. These results indicated that K_2SiO_3 could be used as a new activating agent to produce activated carbon.

1. Introduction

Activated carbons were widely served as a kind of effective adsorbent in wastewater treatment to remove various organic and inorganic pollutants because of their extended surface area, large adsorption capacity and high degree of surface activity [1]. These properties are directly related to the physical and chemical properties of the precursor material, the type of the production method and the production conditions [2]. The influence of activator is crucial in activated carbon preparation. In previous, the traditional activating agents for producing activated carbons were H_3PO_4 [3], KOH [4], K_2CO_3 [5], and $ZnCl_2$ [6]. These activation methods have already been well studied. In recent years, many researchers are interested in finding new activating agents in activated carbon preparations field [7]. According to report, potassium silicate (K_2SiO_3) expresses a kind of strong base and has dehydration function at low temperature. The well flame resistance of K_2SiO_3 was performed at its thermal behavior [8]. Because of these characteristics, use K_2SiO_3 as activating agent to produce activated carbons might be a good method. However, activated carbon prepared with K_2SiO_3 activation has not been thoroughly investigated. The aim of this work was to investigate the influences of activation temperatures and impregnation ratios on pore development of final carbons with PA by K_2SiO_3 activation.

2. Materials and methods

2.1. Materials and chemical reagents

Phragmites australis (PA) as carbon precursor was obtained from the wetland of Nansi Lake area in Shandong Province, China. The precursor was first washed with distilled water to remove surface adhered impurities and then dried at 105 °C for 24 h. The dried PA was crushed and sieved to 40 mesh particle size by standard sieves (Model Φ 200). All chemical reagents were analytically pure.

2.2. Preparation of activated carbons

The PA was impregnated with K_2SiO_3 solution at a certain impregnation ratio (mass of K_2SiO_3: PA, 1.0–2.5). After impregnation for 10 h at room temperature, the sample was transferred into a nickel crucible and heated at temperature of 450–800 °C for 1 h in a muffle furnace. After activation, the products were washed sequentially with hot water, 0.1 N HCl and finally distilled water to

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http://dx.doi.org/10.1016/j.jtice.2014.07.017
1876-1070/

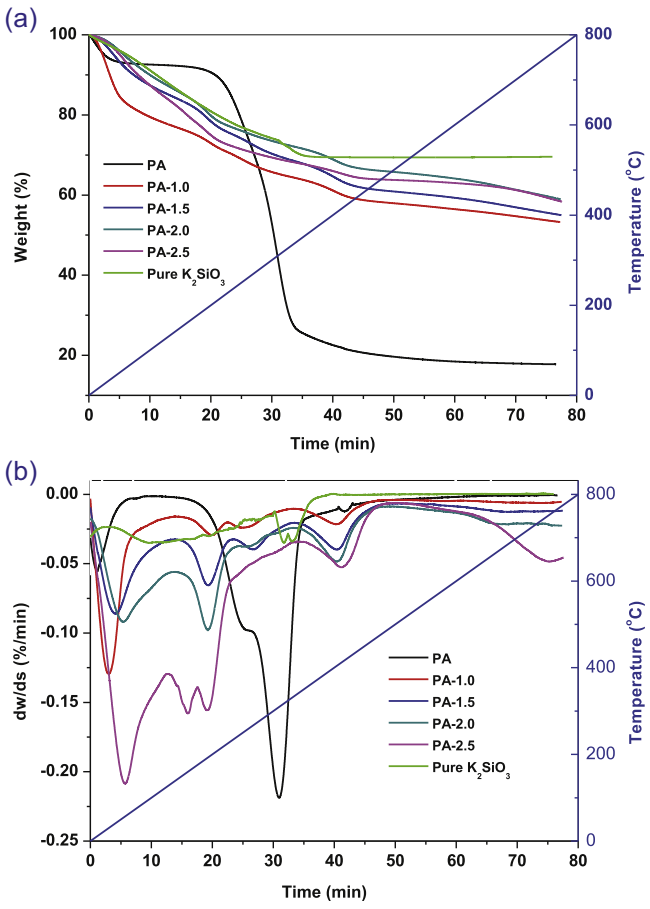

Fig. 1. TGA (a) and DTG (b) curves for the pyrolysis of PA, pure K_2SiO_3 and PA after impregnated with K_2SiO_3.

remove redundancy impurities until neutral pH was obtained. The samples were then dried overnight in a vacuum oven at 105 °C for 10 h, grounded and sieved to 140 mesh particle size by standard sieves (Model Φ 200). The produced activated carbons were referred to as PAC.

2.3. Characterization of activated carbons

Thermo-gravimetric analysis (TGA) and derivative thermo-gravimetric (DTG) curves of samples with different impregnation ratios were obtained by using a thermo-gravimetric analysis (TGA-50 analyzer). The samples were referred to as PA-X and X indicating the impregnation ratio. Each sample was heated in N_2 (100 cm^3/min) atmosphere from room temperature up to 800 °C at a heating rate of 10 °C/min. The surface characteristics of the activated carbons were analyzed using a scanning electron microscopy (SEM; JEOL, JSM 7600F, Japan). The surface areas and pore size distributions of carbons were determined by N_2 adsorption/desorption at 77 K with a surface area analyzer (Quantachrome Corporation, USA).

3. Result and discussion

3.1. Effect of potassium silicate on PA pyrolysis

Fig. 1a and bshows the TGA and DTG curves of PA, K_2SiO_3 and PA treated with K_2SiO_3. Significant changes were detected as a result of the impregnation of K_2SiO_3. It was found that the weight loss was greater in the temperature above 200 °C than PA. This indicated that the impregnation of K_2SiO_3 delayed the main thermal degradation of the raw material and K_2SiO_3 as activator in producing has flame retardance in producing activated carbon.

The TGA and DTG curves of PA alone indicate three mass loss stages: moisture evaporation up to about 110 °C, main devolatilization between 200 and 400 °C, and continuous slight thereafter [9]. However, TGA and DTG curves of the PA impregnated with K_2SiO_3 indicated that the weight loss of these samples solution exhibited four distinct temperature zones. The curves show an initial weight loss for temperature up to 100 °C due to moisture evaporation. The weight loss in the second stage ranged from 150 to 300 °C represented the thermal degradation via pyrolysis of the organic matter in the carbon precursor and dehydration of K_2SiO_3 [8]. In the third stage, the higher amount of mass loss than carbon precursor in the TGA curves as the temperature reached 400 °C may be associated with K_2SiO_3 activation promote the carbonization of lignocellulosic materials. The last stage of activation as the temperature increased 500 °C, the weight loss was slightly. From Fig. 1(b), it is obvious that the weight loss of the K_2SiO_3 was significant from room temperature to 300 °C due to the elimination of moisture and highly volatile matters and of partial dehydration or decomposition of K_2SiO_3. The maximum peak at 350 °C of K_2SiO_3 was observed due to dehydration synthesis. As the temperature increased 500 °C, the weight loss was slightly.

As Fig. 1(a) shows impregnation ratios below 2.0 give rise to weight loss which decreases with increasing impregnation ratio. The possible reason is that the fire resistance of K_2SiO_3 increased with increasing impregnation ratio. For impregnation ratios >2.0 the trend is not anymore discernable. From Fig. 1(b), the sites of the peak of the DTG curves are similarly. But the sizes of the peak increase with increasing impregnation ratio is probably due to the precursors was impregnated sufficient with more activator.

Table 1
Textural parameters and identification of PACs.

Temperature (°C)	Radio	Identification	S_{BET} (m^2/g)	S_{mic} (m^2/g)	S_{mic}/S_{BET} (%)	V_{tot} (cm^3/g)	V_{mic} (cm^3/g)	V_{mic}/V_{tot} (%)	D_p (nm)
450	1.5	PAC-450-1.5	291	181	62.1	0.16	0.08	50.0	2.19
500	1.5	PAC-500-1.5	436	285	65.4	0.246	0.14	56.9	2.26
550	1.5	PAC-550-1.5	513	342	66.7	0.292	0.17	58.2	2.27
600	0	BC	8						
600	1.0	PAC-600-1.0	611	382	62.5	0.298	0.20	67.1	1.95
600	1.5	PAC-600-1.5	721	438	60.7	0.370	0.24	64.9	2.06
600	2.0	PAC-600-2.0	530	409	77.1	0.225	0.16	71.1	1.70
600	2.5	PAC-600-2.5	532	422	79.3	0.279	0.20	71.7	2.10
650	1.5	PAC-650-1.5	678	551	81.2	0.378	0.28	74.1	2.23
700	1.5	PAC-700-1.5	548	477	87.0	0.285	0.22	77.2	2.08
800	1.5	PAC-800-1.5	554	498	89.9	0.271	0.22	80.8	1.96

The Brunauer–Emmett–Teller (BET) equation was used to calculate the surface areas (S_{BET}) of the carbons and the pore size distribution were estimated following the Density Functional Theory (DFT) method. Micropore volume (V_{mic}) and micropore surface area (S_{mic}) were calculated using the *t-plot* method. Total pore volume (V_{tot}) was determined at $P/P_0 = 0.99$. Average pore diameter (D_p) was determined from the relation: $D_p = 4V_{tot}/S_{BET}$.