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Short Communication

Preparation and characterization of activated carbon produced from rice straw by $(\text{NH}_4)_2\text{HPO}_4$ activation

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ABSTRACT

Effects of different pretreatment protocols in $(\text{NH}_4)_2\text{HPO}_4$ activation of rice straw on porous activated carbon evolution were evaluated. The pore structure, morphology and surface chemistry of obtained activated carbons were investigated by nitrogen adsorption, scanning electron microscopy and Fourier transform infrared spectroscopy. It was found that pretreatment combining impregnation with $(\text{NH}_4)_2\text{HPO}_4$ and preoxidation could significantly affect the physicochemical properties of prepared activated carbons. The apparent surface area and total pore volume as high as $1154 \text{ m}^2/\text{g}$ and $0.670 \text{ cm}^3/\text{g}$ were obtained respectively, when combined process of impregnation followed by preoxidation at 200°C and activation at 700°C was carried out. Meanwhile, the activated carbon yield and maximum methylene blue adsorption capacity up to 41.14% and 129.5 mg/g were achieved, respectively. The results exhibited that $(\text{NH}_4)_2\text{HPO}_4$ could be an effective activating agent for producing activated carbons from rice straw.

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1. Introduction

In recent years, the use of low-cost waste, especially agricultural by-products as precursor to prepare activated carbons has attracted much attention due to the high cost in the production of commercial activated carbons from coal, wood and coconut shell. Rice straw is a by-product of rice production. In China, the increasing rice production has permitted production of a large amount of rice straw, which is mostly burned for the purpose of quick disposal and land clearing due to its lower heat value compared with other agricultural residues. In the past 20 years, several researchers began to focus on developing porous activated carbons from rice straw for the removal of pollutants from wastewater. As early as 1991, Kim and Lee (1991) adopted chemical activation with ZnCl_2 as activating agent to produce powdered activated carbons from rice straw for the purification of water. Recently, Basta et al. (2009) applied a two-step process of carbonization followed by KOH activation to prepare activated carbons from rice straw. High-performance activated carbons with surface areas as high as $1917 \text{ m}^2/\text{g}$ were produced.

The study by Benaddi et al. (2000) indicated that activated carbons with high surface areas in the order of $1800 \text{ m}^2/\text{g}$ as well as with well-developed mesoporosity could be produced from wood

using H_3PO_4 as an activating agent. Meanwhile, the authors also performed activation with $(\text{NH}_4)_2\text{HPO}_4$, which had comparable properties of H_3PO_4 , and found the surface area of the obtained activated carbon was $1350 \text{ m}^2/\text{g}$, but the carbon structure was predominantly microporous. Actually, $(\text{NH}_4)_2\text{HPO}_4$ is widely used as a fire retardant due to its ability to lower the pyrolysis and combustion temperature of cellulosic materials (Liodakis et al., 2009). More important, it can cause a considerable increase in the production of mass residue. Nevertheless, to the best knowledge of the authors, there was no work dealing with activation by $(\text{NH}_4)_2\text{HPO}_4$ to produce activated carbons from agricultural wastes. The main purpose of this work is to present the results of activated carbon preparation from rice straw using $(\text{NH}_4)_2\text{HPO}_4$ as an activating agent. The effects of different pretreatment protocols on porous structure, surface properties, adsorption characteristics and yields of the obtained activated carbons were evaluated.

2. Experimental

2.1. Materials

Raw rice straw was first cut into 2–3 cm length and soaked with 2 wt.% NaOH solution for 48 h to remove ash and water soluble substances. The straw was then washed with distilled water until neutrality was reached, and dried and stored for use.

All the reagents were purchased from Shanghai Chemical Reagent Co., China at analytical grade and used without further purification in this study.

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2.2. Preparation of activated carbons

A horizontal tubular carbonization furnace with an artificial intelligence temperature controller HY6000 was used to prepare activated carbons. For thermal treatment, the dried rice straw of 5 g was heated in the furnace under nitrogen atmosphere at an elevating rate of 20 °C/min from room temperature to a specified temperature in the range of 500–800 °C and kept for 1 h. After carbonization, the furnace was cooled under nitrogen to room temperature to prevent re-oxidation of the resulting solids. At last, a washing process was carried out with a solution of 1 mol/L HCl, and then filtrated with a vacuum flask. The solids were thoroughly washed with hot distilled water to remove chloride ions and other residues until the pH of filtrate became neutral. The washed solids were dried 24 h in a vacuum at 105 °C. The final obtained chars were weighed and designated as RS-0.

For chemical activation assays, three protocols were adopted. (i) The dried rice straw of 5 g was first preoxidized under air atmosphere at 200 °C for 2 h, followed by impregnation with 30 wt.% $(\text{NH}_4)_2\text{HPO}_4$ solution using an impregnation mass ratio of 5:1 ($(\text{NH}_4)_2\text{HPO}_4$ /straw); (ii) the dried rice straw of 10 g was first impregnated with $(\text{NH}_4)_2\text{HPO}_4$, and then divided into two equal parts. One half was ready for directly activation, the other was to be (iii) preoxidized under air atmosphere at 200 °C for 2 h. All the three pretreated samples were activated according to the same experimental details as thermal treatment given above. The final obtained solids from (i), (ii), and (iii) were weighed and denoted as RS-1, RS-2 and RS-3, individually. The yield of activated carbon was calculated as Basta et al. (2009).

2.3. Characterization of activated carbons

The weight changes of carbon materials were measured with a NETZSCH Thermogravimetric Analyzer TG 209 F1 Iris in nitrogen at a heating rate of 20 °C/min from 30 to 900 °C. The morphology characteristics of the materials were analyzed by scanning electron microscopy (SEM, JEOL JSM-5600). The functional groups of the products were investigated with Fourier transform infrared spectroscopy (FTIR, Nicolet NEXUS-670).

The pore structure characteristic of all resulting carbon solids was determined by nitrogen adsorption–desorption isotherms at 77 K using Quantachrome NOVAe 4000. The surface area, S_{total} , was calculated by the Brunauer–Emmet–Teller (BET) equation applied at a relative pressure p/p_0 in the range of 0.01–0.20 (El-Hendawy et al., 2001). The total pore volume, V_{total} , was determined at a relative pressure $p/p_0 = 0.95$. The micropore volume, V_{micro} , was calculated by Dubinin–Radushkevich (D–R) equation. The mesopore volume, V_{meso} , was thus calculated by subtracting V_{micro} from V_{total} . The micropore surface area, S_{micro} , was determined by applying D–R method reported by El-Hendawy et al. (2001). The mesopore surface area, S_{meso} , was then calculated by subtracting S_{micro} from S_{total} . The pore size distributions were determined using Battett–Joyner–Halenda (BJH) method. All measurements were assumed the area of a nitrogen molecule to be 0.162 nm².

2.4. Methylene blue (MB) adsorption experiments

Batch experiments were carried out in a set of 250 mL Erlenmeyer flasks, in which a 100 mL aliquot of each MB solution with initial concentration in the range of 50–500 mg/L was added. Equal masses of 0.1 g activated carbons were added to the MB solutions. Each flask was kept in a shaker of 100 rpm at 25 ± 1 °C for 48 h to reach equilibrium of the solid–solution mixture. The concentrations of MB in the solutions were determined using a UV–Vis spectrophotometer (Nicolet UV-2802PCS) at 663 nm wavelength.

3. Results and discussion

3.1. Activated carbon yield

Yields of activated carbons obtained from precursors impregnated with $(\text{NH}_4)_2\text{HPO}_4$ are significantly higher than the carbons without impregnation. At 700 °C, the yield of activated carbon RS-3 (41.14%) is nearly three times higher than that of char RS-0 (15.82%). The possible reason is the formation of higher thermally stable substances from the interaction of $(\text{NH}_4)_2\text{HPO}_4$ with carbon-containing compounds in the rice straw (Ioannidou and Zabaniotou, 2007). The detailed mechanism is not clear at present. From our DTG analysis (not shown here), however, it is notable that there is an evident weight loss at around 639 °C for all the samples of RS-1, RS-2 and RS-3 except for RS-0. This phenomenon has not been reported in other studies with respect to the preparation of activated carbons from rice straw using different activating agents. It may provide partial evidence for the above deduction in regard to the role of $(\text{NH}_4)_2\text{HPO}_4$.

Activation temperature has a great effect on the yields of activated carbons prepared from rice straw with different protocols. Generally, increasing in activation temperature always leads to a considerable decrease of activated carbon yield despite the precursor. This is due to the release of volatile matters through pore opening and biomass gasification during activation at high temperatures. Comparing with the relevant literatures, activated carbon yield 45.12% for RS-3 at 600 °C is higher than for those made from other agricultural wastes with different activation methods under the same activation temperature, such as soybean oil cake of 6.22–16.22% (Tay et al., 2009) and durian peel of 18.74–21.32% (Nuithitikul et al., 2010).

Additionally, the preoxidation process also plays an important impact on the activated carbon yields. The carbon yield of RS-2 (15.59–35.98%) is always lower than that of RS-1 (23.55–44.12%) and RS-3 (37.12–48.99%) at the corresponding activation temperatures. Moreover, at 700 °C, the carbon yield of RS-3 (41.14%) is almost two times as that of RS-2 (22.45%). This influence is attributed to the difference in the strength of the precursor structure resulting from the formation of stable carbon structures during preoxidation treatment, which decreases the gasification intensity of precursors.

3.2. Nitrogen adsorption behavior and porosity development

The nitrogen adsorption–desorption isotherms at 77 K of the obtained carbons and corresponding pore size distribution are shown in Fig. 1. Adsorption and desorption branches show a horizontal plateau over a wide range of relative pressure, indicating the appearance of large fractions of micropores. Fig. 1 and Table 1 clearly show that nitrogen uptake, S_{total} , V_{total} and V_{micro} are significantly increased after impregnation with $(\text{NH}_4)_2\text{HPO}_4$ and preoxidation. The char RS-0 derived by thermal treatment has the lowest S_{total} 351 m²/g and V_{total} 0.168 cm³/g. By contrast, S_{total} and V_{total} of RS-3 are 1154 m²/g and 0.670 cm³/g, respectively. This obvious increase may be resulted from the release of certain volatile compounds generated by impregnation with $(\text{NH}_4)_2\text{HPO}_4$ for the precursors at high temperatures. As a result of this, many new pores of different dimensions are created. Meanwhile, it can be seen that the nitrogen uptake, S_{total} , V_{micro} and V_{total} of RS-2 are all between that of RS-1 and RS-3. This difference demonstrates that preoxidation treatment for precursors before activation plays an important role on the porosity development in carbon matrices. Moreover, the sequence between preoxidation and impregnation is also of great importance. For RS-1, its precursor was pretreated by preoxidation followed by impregnation with $(\text{NH}_4)_2\text{HPO}_4$ before

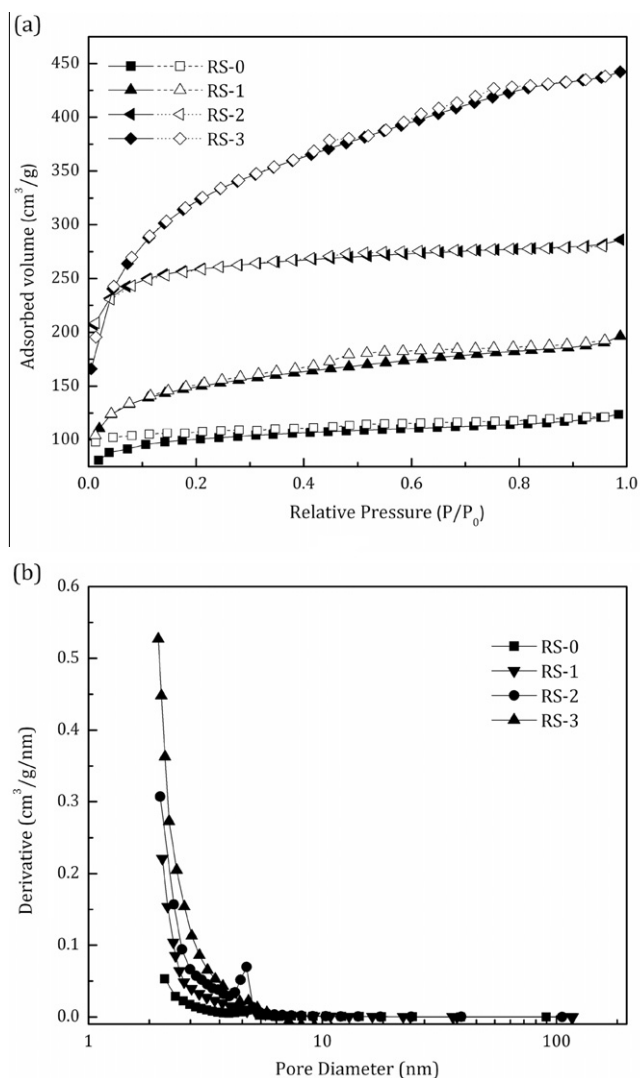


Fig. 1. (a) Adsorption–desorption isotherms of nitrogen at 77 K and (b) pore size distribution of char RS-0 and activated carbons.

activation. Its apparent surface area (BET surface area) and pore volume are both much lower than that of RS-2, which was pretreated in the absence of preoxidation. This may be attributed to the layer of preoxidized products formed on its surface, which hinder the access of $(\text{NH}_4)_2\text{HPO}_4$ to the spaces between the micro-fibrils. On the contrary, the apparent surface area and pore volume of RS-3 are greatly increased after pretreatment with impregnation followed by preoxidation for its precursor. On the other hand, the micropores increase rapidly for RS-1, RS-2 and RS-3 due to the occurrence of pore-opening, and the extent is much greater in RS-3.

Additionally, it can be seen from Fig. 1 that a higher proportion of mesopores with the pore size of about 5 nm are created for RS-2 by contrast with RS-1 and RS-3. It seems that the absence of preox-

idation process can promote the formation of mesopores. In the light of the variation of pore volume among RS-1, RS-2 and RS-3 as shown in Table 1, it is possible to conclude that the introduction of preoxidation is extremely helpful to promote micropore evolution.

3.3. Morphology of activated carbons

From SEM micrographs (not shown here), the surface of raw rice straw is quite smooth. After being soaked, its morphology is attacked due to the interaction of $(\text{NH}_4)_2\text{HPO}_4$ with cellulosic materials of rice straw. The activating agent $(\text{NH}_4)_2\text{HPO}_4$ has comparable properties as H_3PO_4 , thus is able to separate the cellulose fibers as well as produce a partial de-polymerization. Consequently, the chemical can easily invade the spaces between the micro-fibrils and produce a dehydrating effect on the hemicellulose, cellulose and lignin components. Moreover, $(\text{NH}_4)_2\text{HPO}_4$ molecules can remain inside acting as a template for creating micropores during the following activation. After preoxidation at a temperature of 200 °C under air atmosphere, some cracks can be seen on the surface of rice straw. Normally, hemicellulose components of lignocellulosic materials begin degrading over a temperature range of 150–350 °C, and cellulose decomposes under an air atmosphere at a temperature above 250 °C (Aggarwal et al., 1997; Kumer and Pratt, 1996). However, the study by Major (Major, 1958) indicated that cellulose started to be oxidized over a temperature range of 170–185 °C, which is an apparent contradiction of the results obtained from other studies. As a result, the morphology change of rice straw after preoxidation at a temperature of 200 °C is probably due to the partial decomposition of both hemicellulose and cellulose components, but the detailed mechanism needs further investigations.

3.4. Surface chemistry of activated carbons

Compared with raw rice straw, the number of C–O vibration absorption peaks of the derived activated carbons at bands around 1400 cm^{-1} is increased. The appearance of weak vibrations at bands between 2510 and 2348 cm^{-1} for RS-1 and RS-3 is probably attributed to C=O vibrations in ketene and carboxyl groups.

3.5. MB adsorption analysis

Batch adsorption experiments using MB as an adsorbate are frequently performed to test the adsorption performance of obtained activated carbons. In the present study, the experimental data exhibit that the maximum MB adsorption uptakes for RS-1, RS-2 and RS-3 are 124.5, 59.9 and 129.5 mg/g, respectively. By contrast, the MB adsorption capacity of RS-3 is higher than that of all the activated carbons prepared from rice straw with H_3PO_4 activation by Fierro et al. (2010).

4. Conclusions

Different pretreatment protocols consisting of impregnation with $(\text{NH}_4)_2\text{HPO}_4$ and preoxidation were demonstrated to affect

Table 1
Apparent surface area and pore volume of the carbons obtained at 700 °C.

Type of carbon	Apparent surface area (m^2/g)			Pore volume (cm^3/g)			Pore volume distribution (%)		Mean pore width (nm)
	S_{micro}	S_{meso}	S_{total}	V_{micro}	V_{meso}	V_{total}	$V_{\text{micro}}/V_{\text{total}}$	$V_{\text{meso}}/V_{\text{total}}$	d
RS-0	218	133	351	0.115	0.071	0.186	61.83	39.17	1.91
RS-1	340	185	525	0.187	0.104	0.291	64.26	35.74	2.22
RS-2	588	314	902	0.280	0.152	0.432	64.81	35.19	1.92
RS-3	751	403	1154	0.434	0.236	0.670	64.78	35.22	2.32

the physicochemical properties of prepared activated carbons significantly. High-performance activated carbons were prepared with apparent surface area, total pore volume and maximum MB adsorption capacity as high as 1154 m²/g, 0.670 cm³/g and 129.5 mg/g, respectively, when the combined process of impregnation with (NH₄)₂HPO₄ followed by preoxidation at 200 °C and activation at 700 °C was carried out. Additionally, the carbon yield was improved considerably. This work confirmed the relevance of pre-treatment protocols and (NH₄)₂HPO₄ activation in the production of porous activated carbons from waste rice straw.

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