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Rice straw as precursor of activated carbons: Activation with ortho-phosphoric acid

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ABSTRACT

Highly mesoporous activated carbons (ACs) with a mesopore fraction ranging from 42 to 73% were obtained by activation of rice straw (RS) with ortho-phosphoric acid (PA). Due to such a high mesoporosity, these ACs can be successfully used for pollutant removal in aqueous phase. The ACs were prepared at activation temperatures (T) ranging from 350 to 500 °C, using PA to RS weight ratios (R) from 0 to 1.6 and activation times from 0 to 2 h. They were characterised by nitrogen adsorption at −196 °C, SEM-EDX, and methylene blue adsorption. RS is a very heterogeneous material with a variable content of mineral matter: using the product of activated carbon yield multiplied by surface area ($C \times S_{BET}$) as the performance criterion, the best AC was produced at $T = 450$ °C and $R \geq 1$. These conditions lead to S_{BET} higher than 500 $m^2\ g^{-1}$ and a $C \times S_{BET}$ around 270 $m^2\ g^{-1}$.

1. Introduction

Three million tons of rice straws (RS) are produced annually in Egypt. So far, such a resource is mainly considered as a waste, and consequently burnt without any profit, except in a few cases of domestic uses for cooking and heating. Worse, biomass burning is a major source of atmospheric pollution [1], especially through the fumes and the very fine silica particles thus produced, both having a suffocating effect. Although wildfires are prohibited in cultivation fields of most countries, farmers usually keep on burning their crop by-products.

Rice-derived wastes comprise two different materials: husks and straws. Rice husks have been commonly investigated as potential precursors of ACs [2–4]. By contrast, straws have been seldom suggested for this application, whereas other routes of valorisation have been considered in the past, e.g., pulp and paper, construction materials, compost, fuel, production of chemicals such as ethanol and bio-adsorbents [5] and references therein.

To the best knowledge of the present authors, only three works have been carried out using RS as AC precursor, based on chemical activation by potassium hydroxide on one hand [5,6], and by sodium hydroxide on the other hand [7]. In our previous paper [5], three pre-treatment protocols were tested: mechanical, chemical (by NaOH pulping), and a combination of both, followed by a further activation with KOH according to either one or two steps. Employing the combined mechanical–chemical pre-treatment method and a 2-steps KOH activation process, surface areas as high as 1917 $m^2\ g^{-1}$ could be obtained. However, the use of such complex activation protocol working at temperatures as high as 800 °C makes RS-based AC production rather expensive.

Ortho-phosphoric acid (PA), H_3PO_4, is a common activating agent whose use has been extensively reported for preparing activated carbons from agricultural by-products [8–12], wood [13,14], natural [15,16] as well as synthetic [17,18] carbons. PA promotes the bond cleavage in the biopolymers and dehydration at low temperatures [19], followed by extensive cross-linking that binds volatile matter into the carbon product and thus increases the carbon yield. Benaddi et al. [20] showed that the mechanism of PA activation of biomass feedstock occurs through various steps: cellulose depolymerisation, biopolymers dehydration, formation of aromatic rings and elimination of phosphate groups. This allows activated carbons to be prepared with good yields and high surface areas. Activation conditions thus depend on the nature of the precursor, i.e., on the relative amounts of cellulose, hemicellulose, lignin and ashes. For example, the present authors already prepared ACs from lignin (L) by activation with H_3PO_4, and the optimum PA/L weight ratio allowing complete reaction of lignin has been

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Table 1
Activation conditions for RS impregnated with H_3PO_4.

Sample name	Impregnation ratio	Impregnation time (h)	Heating rate (°C min^{-1})	Activation time (h)	Temperature (°C)
R effect (t_a = 2 h and T = 450 °C)					
R000	0	1	5	2	450
R025	0.25	1	5	2	450
R050	0.5	1	5	2	450
R075	0.75	1	5	2	450
Reference	1	1	5	2	450
R120	1.2	1	5	2	450
R140	1.4	1	5	2	450
R160	1.6	1	5	2	450
t_a effect (R = 1 and T = 450 °C)					
AT0	1	1	5	0	450
AT1	1	1	5	1	450
T effect (R = 1 and t_a = 2 h)					
T350	1	1	5	2	350
T375	1	1	5	2	375
T400	1	1	5	2	400
T425	1	1	5	2	425
T475	1	1	5	2	475
T500	1	1	5	2	500

evidenced at a value around 1.0. Further increase of PA/L did not produce changes of weight loss during pyrolysis, and hence no change of carbon yield occurred [21]. From the point of view of porosity development, the optimal PA/L weight ratio was found to range from 1.2 to 1.4, leading to ACs having high surface areas (1300 m^2 g^{-1}) and porosity (0.7 cm^3 g^{-1}) [22].

Given the composition of RS, rich in cellulose and ashes, rather different optimal experimental conditions are thus expected for preparing the best possible adsorbents. The objective of this work was to describe for the first time the properties of RS chemically activated with ortho-phosphoric, and to find the best experimental conditions for obtaining ACs having both with high surface areas and carbon yields.

2. Experimental

2.1. Rice straw characterisation

The contents of α-cellulose, pentosan and lignin have been determined according to methods detailed elsewhere [5]. The average ash content in RS was calculated by weighing a number of samples before and after all the organic matter was burnt by heating in a muffle furnace up to 600 °C (ASTM E1755-01).

2.2. Synthesis of ACs

Rice straw (RS) was impregnated with phosphoric acid (PA) for 1 h using PA to RS weight ratios, *R*, ranging from 0.25 to 1.6. The resultant mixture was introduced in a quartz tube and placed inside a quartz tubular reactor. The latter was placed in a vertical oven, heated at 5 °C min^{-1} up to the final activation temperature, which was held for activation times, t_a, ranging from 0 to 2 h under nitrogen flow. Once the activation was finished, the oven was switched off and the carbonised material let to cool under nitrogen flow. The resultant AC was washed with distilled water in a Soxhlet for 5 days, and then dried overnight in an oven at 105 °C. Table 1 lists the activation conditions and the corresponding name of the ACs thus prepared. The sample synthesised at 450 °C with an activation time of 2 h and a ratio PA/RS of 1 is referred to as the "reference" sample in the following. It is the one to which any other material prepared in different experimental conditions will be compared. According to the nomenclature of Table 1, the reference sample might be also called R100, AT2, or T450.

2.3. Characterisation of ACs

2.3.1. Electron microscopy

The morphology of activated RS samples has been observed by Scanning Electron Microscopy (FEG-SEM Hitachi S 4800) equipped with an EDX (Energy Dispersion of X-rays) instrument. The latter was used for the semi-quantitative analysis of the ashes.

2.3.2. Nitrogen adsorption at −196 °C

The pore texture parameters have been determined from the corresponding nitrogen adsorption–desorption isotherms obtained at −196 °C with an automatic instrument (ASAP 2020, Micromeritics). The samples were previously outgassed at 250 °C for 24 h. The surface areas were determined by the BET calculation method [23] applied to the adsorption branch of the isotherms. The micropore volume, V_{DR}, was calculated according to the Dubinin–Radushkevitch method [24]. The total pore volume, sometimes referred to as the so-called Gurvitch volume, $V_{0.99}$, was defined as the volume of liquid nitrogen corresponding to the amount adsorbed at a relative pressure p/p_0 = 0.99 [25]; the Gurvitch volume is assumed to be the sum micropore + mesopore volumes. The mesopore volume, V_{meso}, was thus calculated as the difference between $V_{0.99}$ and V_{DR}.

2.3.3. Ash content determination

Ash content in ACs was determined in a thermogravimetric device (TAG 1750, Setaram). 20 mg of AC were heated in air according to the following temperature program:

(i) Moisture was measured by the weight loss of the sample heated at 5 °C min^{-1} up to 105 °C, the final temperature being held for 30 min.
(ii) Ash content was next determined on a dry basis by heating the resultant sample at 5 °C min^{-1} from 105 to 650 °C. The latter temperature, chosen according to the D2866-94 ASTM standard (i.e., relevant to activated carbons), was maintained for 60 min.
(iii) Finally, additional heating at 5 °C min^{-1} from 650 to 815 °C was carried out, the latter temperature being maintained for 60 min and now chosen on the basis of the ISO standard 1171 (i.e., corresponding to mineral carbons).