Comparative study on characterization and adsorption properties of activated carbons by phosphoric acid activation from corncob and its acid and alkaline hydrolysis residues

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ABSTRACT

Four activated carbons were prepared from corncob, acid hydrolysis residue, alkaline hydrolysis residue and China fir sawdust respectively with phosphoric acid activation under the same process condition. TG/DTG-DSC analysis revealed that the addition of phosphoric acid decreased the pyrolysis rate while increased the temperature and the yield. The findings showed that the acid and alkaline hydrolysis residue from corncob were both suitable to prepare high performance activated carbon. Moreover, different micropore volume, mesopore volume and mean pore width existed although activated carbons possessed the similar BET surface area and total pore volume. In addition, the liquid phase adsorption and pore properties of activated carbons were contrasted to show that the pore structure varied from one to another though with more or less the same iodine number, methylene blue adsorption and decolorization of caramel. Compared to China fir sawdust, activated carbons from corncob, acid hydrolysis residue and alkaline hydrolysis residue were easily made with a high decolorization of caramel. FTIR results suggested that four activated carbons were found with hydroxyl and phosphorus groups.

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1. Introduction

The rapid growth of Chinese economy has worsened the environmental pollution, also accompanied with the call for the construction of ecologically civilized society. The most stringent Chinese Environmental Protection Law was in force since January 1st of 2015, which in turn urged pollution-makers to impose more controls on the discharge of waste gas and waste water. Activated carbon (AC) is an efficient material for the control of environment pollution, which is extensively applied in liquid-phase and gas-phase pollution. Concerning the emergency above, the potential use of AC is expected to rise substantially in the near future. Currently, our production of wooden AC by phosphoric acid is primarily sourced from pine and China fir sawdust in wood processing. The output of the sawdust, however, is a limited source and also selected as the raw and auxiliary materials in many other industries. In a response to the large potential demand for AC, it is quite important to tailor and develop more biomass materials for AC production by phosphoric acid method. For a decade or more, many studies had focused on AC preparation by phosphoric acid from agriculture and forestry wastes, such as cotton stalks [1–2], *Arundo donax* cane [3], tobacco stems [4], sugar cane bagasse [5], sunflower seed hull [5], globe artichoke leaves [6], *Cyperus alternifolius* [7], *Acacia mangium* wood [8], date stems [9], date (*Phoenix dactylifera* L.) stone [10], reedy grass leaves [11], cocoa shells [12], siriguela seeds [12], etc.

Furfural is an important chemical material. Residual wastes of agricultural by-products with a large amount of pentosan, including corncob, peanut shell, sorghum husk and sugar cane bagasse are chosen as materials for the production of furfural. Residual solid after the extraction of furfural is called furfural residue. Corncob is widely used as the material to produce furfural due to its higher furfural yield. 12–15 tons of furfural residues are left in 1 ton of furfural output. It is estimated that 3 million tons of furfural residues are produced per year in China [13–15]. Many furfural residues are exposed to open air, which not only occupy a large area of land but also cause a complication of environmental concerns, gradually becoming the bottleneck of furfural industrial cycle development. Thus, the resource utilization desperately calls for the rational utilization of furfural residues and the elimination of its environmental pollution. This implies a critical task and urgent need to improve the value-added of furfural residues in order to achieve the objective of clean production and cyclic utilization. As a biomass waste with a lot of cellulose and lignin, furfural residues are usually preferred for its good recycling use. Nowadays, they are primarily used for making activated carbons (ACs) [14–16], conditioning the soil [17], extracting the cellulose [18–19], preparing the fuel ethanol [20] and

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Nomenclature

CAF	Chinese Academy of Forestry
SFA	State Forestry Administration
ACs	activated carbons
CB	corncob
AHR	acid hydrolysis residue
KHR	alkaline hydrolysis residue
CFS	China fir sawdust
TG	thermogravimetry
DTG	differential thermogravimetry
DSC	differential scanning calorimetry
AHR-AC	activated carbon prepared from acid hydrolysis residue
BET	Brunauer–Emmett–Teller
KHR-AC	activated carbon prepared from alkaline hydrolysis residue
CB-AC	activated carbon prepared from corncob
CFS-AC	activated carbon prepared from China fir sawdust
FTIR	fourier transform infrared
AC	activated carbon
GB/T	China recommendatory national standard
SEM	scanning electron microscope
CB-P	a mixture of corncob and H_3PO_4
AHR-P	a mixture of acid hydrolysis residue and H_3PO_4
KHR-P	a mixture of alkaline hydrolysis residue and H_3PO_4
CFS-P	a mixture of China fir sawdust and H_3PO_4
Ads.	adsorption
Des.	desorption
S_{BET}	BET surface area
V_{tot}	total pore volume
$V_{mic,DA}$	micropore volume calculated by D-A equation
DFT	density function theory
V_{mes}	mesopore volume
D_m	mean pore width IUPAC
	International Union of Pure and Applied Chemistry

using as fuel, etc. In this work, powdered ACs will be prepared from corncob (CB), acid hydrolysis residue (AHR), alkaline hydrolysis residue (KHR) and China fir sawdust (CFS) by two-step approach with phosphoric acid.

2. Experimental

2.1. Preparation of ACs

AHR (moisture content: 73.15%), KHR (moisture content: 75.94%) kindly provided by Shandong Shengquan Group and CFS (moisture content: 38.62%) from Yushan Sanqing Activated Carbon Co., Ltd. were dried until the moisture content was about 20%, while CB (moisture content: 5.54%) from Shandong Shengquan Group needn't to be dried. AHR was weighed in 20 g and placed in the beaker, and then mixed with the phosphoric acid solution (mass fraction: 60%) in the impregnation ratio of 2:1. After evenly stirring, the mixture was put into the stainless steel container without cover with a height of 2 cm, kept in the oven at 270 °C for 1 h. Subsequently, the mixture was moved to the porcelain crucible, covered and placed in the muffle furnace at 450 °C for 1 h. The heating rate was 10 °C min^{-1}. After the activation, the porcelain crucible was immediately removed from the furnace and cooled to the ambient temperature. Finally, the activated sample was cleaned with hot water for several times until the filtrate was at pH 3 ~ 5 and then the filter residue was placed in the oven at 150 °C for 10 h. The AC was ground and filtered through the 200 mesh and denoted to AHR-AC. Under the same technical condition, ACs were labeled as CB-AC, KHR-AC and CFS-AC from CB, KHR and CFS, respectively.

2.2. Analytical Methods

Lignin and pentosan content in CB, AHR, KHR and CFS were determined as per GB/T 2677.8-1994 and GB/T 2677.9-1994 respectively while cellulose content was determined using nitric acid-ethanol method [21].

Iodine number, methylene blue adsorption and decolorization of caramel of ACs were determined as per GB/T 12496.8-1999, GB/T 12496.10-1999 and GB/T 12496.9-1999 respectively.

The surface morphology of raw materials were observed under 3400-IScanning Electron Microscope (SEM) at accelerating voltages of 15 kV and amplified by a factor of 1000. Before observation, the samples were coated with gold in E-1010 Ion sputter.

Pyrolysis of four raw materials (CB, AHR, KHR and CFS) and the corresponding H_3PO_4-impregnated materials (CB-P, AHR-P, KHR-P and CFS-P) were carried out by 409PC simultaneous thermal analyzer. Samples were weighed (raw materials: 4 mg, H_3PO_4-impregnated materials: 15 mg) and placed in the alumina crucible and then moved the crucible on the micro balance. Air was chosen as the reactant gas at the airflow rate of 35 ml min^{-1} and then samples were heated from 40 to 800 °C at the heating rate of 10 °C min^{-1}. The TG, DTG and DSC curves were recorded simultaneously as the temperature increased.

The N_2 adsorption–desorption isotherm determination of AC was carried out in ASAP 2020 at 77 K. BET surface area (S_{BET}) of AC was calculated based on BET equation and total pore volume (V_{tot}) was calculated by the adsorption quantity at the relative pressure of 0.975. Micropore volume ($V_{mic,DA}$) was calculated by D-A equation. Pore size distribution of AC was identified by Density Function Theory (DFT) method.

The surface chemical property of AC was analyzed using iS10 Fourier transform infrared (FTIR) spectrometer. AC sample was ground to a particle size (<45 μm) and dried at 150 °C for 10 h and then prepared in the form of KBr pellets with the sample to KBr ratio 1:100. The frequency range was selected in the region of 4000 to 400 cm^{-1}.

3. Results and discussions

3.1. SEM image and biological components

As shown in Fig. 1, both CB and CFS maintain the complete biological structure. CB is found with a disordered, amorphous and multi-branch construction due to its bigger content of pentosan [22]. However, CFS is found with a densely ordered, regular and multi-porous construction. In addition, AHR and KHR, which are the residues after furfural is extracted from CB through acid and alkali hydrolysis respectively, are found with irregular, multi-porous and fluffy construction.

It is obvious that pentosan content in CB is higher than that in CFS (Fig. 2). With regard to AHR and KHR, the pentosan content substantially decreases after acid or alkali hydrolysis, especially for KHR. The cellulose content in AHR and KHR is significantly higher than that in CB and CFS. Nevertheless, the lignin in CFS is far higher than that in three other raw materials.

3.2. TG/DTG-DSC

It has been reported that wood pyrolysis is the most intense within the temperature range: 200–320 °C for hemicellulose, 280–400 °C for cellulose and 140–900 °C for lignin [22–23].

TG/DTG-DSC curves of these four raw materials suggest three stages of weight loss in the pyrolysis process of these four materials exposed to air (Fig. 3). The weight loss of the first stage (40–200 °C) is primarily due to water evaporation.

The weight loss of the second stage (200–400 °C) is mostly ascribed to the pyrolysis of cellulose and hemicellulose as well as a few lignins. It is observed from the TG curves that the pyrolysis loss of CB, AHR, KHR and CFS is 60.3%, 67.0%, 67.5% and 61.7% respectively in the first two