

Synthesis of Microporous-Mesoporous Carbons from Rice Husk via H₃PO₄-Activation

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Abstract. Highly porous activated carbons were prepared through chemical activation of rice husk (RH). For the sake of optimization of the process, sixteen activated carbon samples were obtained from RH by means of carbonization in presence of H₃PO₄, and successive alkaline desilication, at the following conditions: activation time– 0.5 to 2 h, temperature– 300 to 600 °C and H₃PO₄/RH (wt/wt) impregnation ratio– 0.5 to 2. Samples were analyzed according to the data of thermal desorption of argon, low-temperature N₂ adsorption using BET equation and BJH-calculation scheme, methylene blue (MB) adsorption studies, SEM, elemental analyses and yields. N₂-BET surface area reached the value of 1690 m²/g; maximal MB adsorption capacity– 667 mg/g.

Introduction

Rice husk (RH), a by-product of rice milling industry, is a renewable waste with the annual world production over 545 million tons [1]. Even though RH is used as a fuel in the rice producing countries, it is characterized by low caloric value and high mineral content [2]. On the other hand, RH as a lignocellulosic biomass is a valuable carbonaceous precursor that can be used to obtain a carbon material with special textural properties, high specific surface area and large pore volume [3, 4]. Highly mesoporous carbons with relatively low surface area and total pore volume were obtained from RH through a two-stage process (precarbonization followed by H₃PO₄ activation in temperature range of 700–900 °C) [5]. Activated carbon with BET surface area and total pore volume as high as 874 m²/g and 0.713 cm³/g was also prepared from RH by H₃PO₄ activation [6]. Yet, high mineral content of activated carbons prepared from RH by H₃PO₄ activation, which is within range of 20–70%, restricts their commercial use. In a multitude of previous studies on H₃PO₄ chemical activation of lignocellulosic materials it has been suggested that the use of inert atmosphere is necessary and that the optimal conditions to attain highest surface area are: 0.5 to 2 h of activation time, 450-550 °C and H₃PO₄/precursor (wt/wt) impregnation ratio of ca. 1-2. To elucidate the trends of how these parameters affect the yield, specific surface area and pore structure of carbonized rice husk (CRH), reasonably broader ranges of activation parameters were chosen and a two-step H₃PO₄ activation-desilication process (acid/base treatment) was applied to a pseudo-random selection of sixteen RH samples.

Materials and methods

Chemical activation technique

Synthesis of carbonized materials (CRH) was accomplished via successive procedures of precarbonization of rice husk with H₃PO₄, activation at 400-600 °C in self-generated atmosphere, followed by neutralization, desilication, washing and drying. At first, sixteen glass jars having 30 grams of rice husk each and the appropriate amount of admixed 70% H₃PO₄ (ρ=1.54 g/cm³) were placed into an oven and heated at 200 °C overnight. Precarbonized contents of the jars were transferred into quartz test tubes and loosely covered with stoppers (4 series of 4 test tubes). A series of 4 test tubes with the material impregnated at different ratio (IR) s was placed into a

vertical cylindrical furnace equipped with chromel/alumel thermocouple. Each time a series was heated at the rate of about 5 °C/min to a desired temperature and the temperature was maintained for 2 hours. Every half hour a test tube was removed from the furnace. To expedite washing, each carbonized residue was neutralized to Na₂HPO₄ with the equivalent amount of concentrated NaOH solution and refluxed for 10 min. Then, carbonaceous precipitates were boiled for 30 minutes in 2 L of 1.2 M NaOH and washed again till neutral pH. Samples were dried in hot air oven at 110±5 °C.

Thermal desorption of argon and low-temperature nitrogen adsorption

The specific surface area (SSA) of the samples was determined by argon thermal desorption using analyzer SORBI N.4.1. Information on microporous and mesoporous texture (range from 17 to 3000 Å) was obtained by the method of low-temperature nitrogen adsorption using “ASAP-2400” Analyzer (Micromeritics Instrument Corp., Norcross, GA, USA), upon pretraining of the samples at 150°C and residual pressure of 0.001 mm Hg.

Methylene blue adsorption

The desired concentrations for methylene blue (MB) adsorption studies and calibration solutions for spectrophotometric evaluation were obtained by successive dilution of aqueous MB stock solution (4000 mg/L). Each time a 50 ml glass-stoppered flask with 0.10 g activated carbon and twenty-five milliliters of a dye solution added was placed on a magnetic stirrer at room temperature for 20 min. Then the absorbance of supernatant solution was estimated to determine the residual concentration.

MB adsorption capacity q_e was calculated from the mass balance equation: $q_e = \frac{(C_0 - C_e) \cdot V}{m}$,

where C_0 and C_e are the initial and equilibrium dye concentrations, V is the volume of liquid phase and m — mass of adsorbent. Obtained adsorption isotherm data were plotted in the linear Langmuir-isotherm model [4]: $\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}}$, where q_{\max} is MB-monolayer capacity and K_L is a constant

related to adsorption free energy. For methylene blue (MB) number determination, 25 ml of 1500 mg/L stock solution was added to 0.1 g of a carbon according to the technique described above; therefore the maximal theoretical MB-number (adsorption capacity q_e) is 375 mg/g.

Elemental analysis

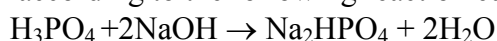
Analyses of mineral part of the samples were performed using X-ray fluorescence spectroscopy on VRA-30 analyzer with Cr-anode X-ray tube; as well as using energy-dispersion analyzer “SPRUT-001”. Carbon, hydrogen and nitrogen contents were determined by use of elemental analyzer “VARIO ELEMENTAR III”.

Scanning electron microscopy

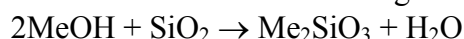
The morphology of activated carbons was studied by scanning electron microscopy (SEM) using QUANTA 3D 200i microscope (FEI, USA) with accelerating voltage of 30 kV.

Results and Discussion

In our previous experience with H₃PO₄ activated CRH we found that it takes unreasonably long time to get rid of H₃PO₄ by simply washing it with distilled water: SiO₂ species formed in presence of H₃PO₄ at high temperatures (600 °C) continuously washed out from carbon matrix in colloidal form. Knowing that Na₂HPO₄ is about neutral, to facilitate and expedite such a meticulous washing process, we used neutralization according to the following reaction equation:



In the case of silicon containing carbon composites, the use of alkaline agents, such as NaOH or KOH is an extra way to obtain mesoporous materials due to washing out from the matrix the water-soluble sodium or potassium silicates that are formed according to the reaction equation:



where Me is Na or K, and SiO₂ serves as a template for pore formation. We also tried to find out how range variation of the activation conditions, specifically: temperature, impregnation ratio (IR) or wt/wt-IR (H₃PO₄/RH) and carbonization duration, affect carbon yield, surface area (S_{BET}) and MB-number of activated carbons. Summarized data are presented in table 1.

Table.1. Effect of activation parameters on Ar-BET surface area, MB-number and carbon yield

Sample number	T [°C]	IR	t [h]	S _{BET(Ar)} [m ² /g]	Yield [%]	MB-number [mg/g]
1	300	0.5	0.5	210	42.2	95
2	300	1.0	1.5	430	39.0	97
3	300	1.5	1.0	770	32.5	127
4	300	2.0	2.0	1150	26.7	193
5	400	1.5	0.5	1600	30.6	300
6	400	2.0	1.5	2300	26.1	367
7	400	0.5	1.0	550	32.8	135
8	400	1.0	2.0	1760	32.2	300
9	500	1.0	0.5	1070	32.1	362
10	500	1.5	1.5	1730	30.0	370
11	500	2.0	1.0	2490	26.6	371
12	500	0.5	2.0	670	32.5	140
13	600	2.0	0.5	2010	33.2	368
14	600	0.5	1.5	870	35.3	130
15	600	1.0	1.0	1670	40.1	255
16	600	1.5	2.0	2150	31.0	308

The results shown in table 1 apparently suggest that:

- 1) out of the three activation parameters, IR has the strongest effect and at IR of 2, S_{BET} is the highest, while at 0.5– is the lowest in each series: compare samples 4, 6, 11, 13 with 1, 7, 12, 14;
- 2) time and temperature seem to have less effect in general at the chosen range, however for sample 4 obtained at 300 °C even 2 h of carbonization is not enough to reach S_{BET} value of the sample 5 (1150 m²/g vs. 1600 m²/g) heated at 400 °C for only half hour, although impregnated at lesser value (1.5 vs. 2). On the other hand when it comes to sample 13 in comparison with sample 6 (400 °C, 1.5 h, both impregnated at the same ratio of 2), 0.5 h of activation time at 600 °C is seemingly not enough to undergo sufficient carbonization, in terms of lower S_{BET} value.

Table.2. Elemental composition according to data of X-ray fluorescence spectroscopy and “VARIO ELEMENTAR III” analyzer* of CRH samples and their adsorption/textural properties.

Sample number	4	6	11	13
T [°C]	300	400	500	600
wt/wt-IR (H ₃ PO ₄ /RH)	2	2	2	2
t [h]	2	1.5	1	0.5
Yield [%]	26.7	26.1	26.6	33.2
C* [%]	72.98	87.88	87.96	78.33
N* [%]	0.3	0.2	0.26	0.51
H* [%]	2.95	2.42	1.92	1.92
C,H,N,O [%]	99.15	99.49	99.00	97.29
O [%]	~23.0	~9.0	~8.8	~16.5
P [%]	0.77	0.41	0.89	2.44
Si [%]	0.027	0.034	0.037	0.088
Max.MB-layer capacity[mg/g]	309	667	562	442
S _Σ [m ² /g]	964	1476	1690	1552
S _μ [m ² /g]	420	0	0	196
V _Σ [cm ³ /g]	0.6	1.5	1.95	1.17
V _μ [cm ³ /g]	0.2	0	0	0.094
D _{ave} [nm]	1.8	4.0	4.4	3.0

CRH samples with highest S_{BET} in each series, e.g.: samples 4, 6, 11 and 13, were further analyzed by different physicochemical methods of investigation: low-temperature N_2 adsorption studies, methylene blue adsorption studies to determine MB-monolayer capacity (q_{max}) using linear Langmuir-isotherm model, elemental analyses using elemental analyzer “VARIO ELEMENTAR III” and X-ray fluorescence spectroscopy to determine organic and inorganic content of the samples respectively. These samples pore size distribution and textural properties are shown in Fig.1 and Table 2. The standard calculations for N_2 -adsorption isotherms were performed by Barret-Joyner-Halenda method, with the admission of postulated model for cylindrical pores, the calculation of total pore surface area S_{Σ} and micropore surface area S_{μ} by BET-method, total pore volume V_{Σ} and micropore volume V_{μ} ; average pore diameter D_{ave} (inclusive of micro- and mesopores). According to these results, the largest portion of pores is accounted for mesopores, these pores volume and surface area may be calculated by subtraction of the values of micropore volume and surface area from corresponding total values (Table 2). At the same time substantial amount of micropores are present in the samples 4 and 13. Mesopore size is mainly about 4 nm and the pore size ranges from 3 to 40 nm (Fig.1).

Elemental analysis of the samples 4, 6, 11 and 13 showed traces of ash elements, considerably large amount of phosphorus (most probably due to formation of phosphate groups covalently bonded to carbon matrix), and only small amounts of remaining silica, which indicates successful desilication. Highest carbon content for the samples 6 and 11 compared to samples 4 and 13 indicates higher degree of carbonization and correlates with high surface area and pore volume.

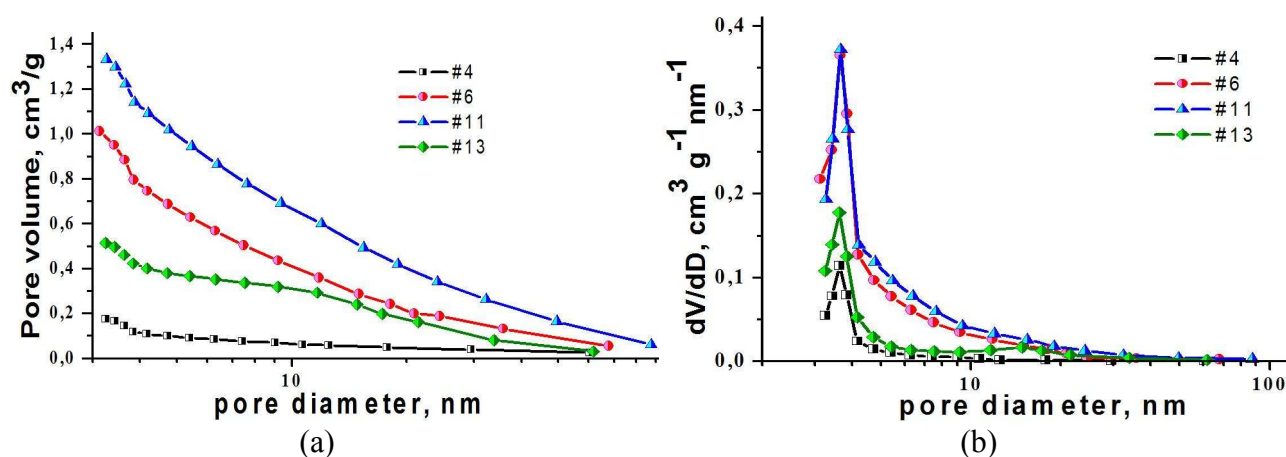


Fig.1. Integral (a) and differential (b) pore size distribution in CRH samples 4, 6, 11 and 13

MB batch adsorption studies results at equilibrium conditions fitted linear Langmuir-isotherm model with high R^2 values, up to 0.995. Large values of maximal MB-monolayer capacity (q_{max}) of CRH samples shown in Table 2, also suggest high mesoporosity, since the MB molecule is accessible to the pores with diameters larger than 1.5 nm [7]. However it is unclear why sample 6, having lower N_2 -BET surface area ($1476 \text{ m}^2/\text{g}$), exhibits larger maximal MB layer capacity (667 mg/g) compared to sample 11 with the corresponding values of $1690 \text{ m}^2/\text{g}$ and 562 mg/g . A possible explanation lies in the fact that not all pores are accessible to both adsorbates, e.g.: some mesopores may be “closed” and/or inaccessible to MB molecule due to their shape (structure) having narrowings smaller than the cross-sectional area of MB molecule.

Scanning electron microscopic pictures of the CRH sample 11 are shown in Fig.3. From SEM images on Fig.2a, it is evident that the texture of carbonized sample retained native RH morphology despite harsh chemical (acid-base) treatment. Porous surface of CRH sample 11 shown in Fig.2b, has nanoscale structural elements (pores) of a size of tens of nanometers. Native RH structure retention could be attributed to the presence of high amount of silica in the starting material and the sequence of acid-base treatment.

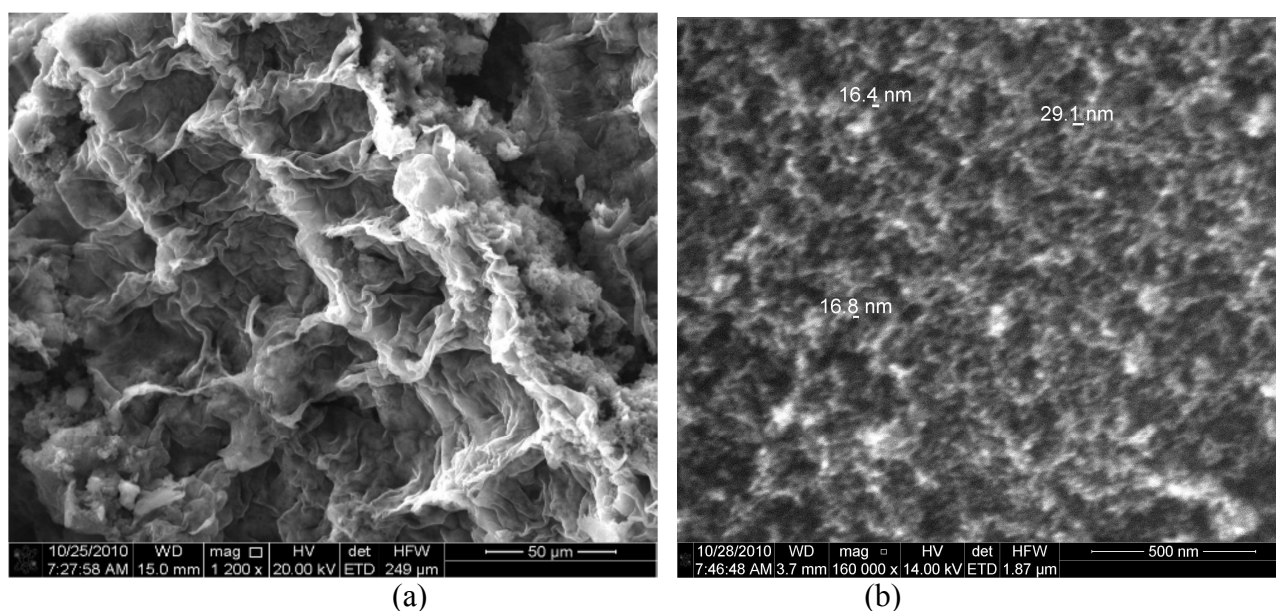


Fig.2. SEM images of CRH sample 11 at magnification:
(a) – x 1 200; (b) –x 160 000

Conclusions

Novel microporous-mesoporous carbons derived from rice husk were synthesized by carbonization in the presence of phosphoric acid as activating agent in self-generated atmosphere, followed by alkaline desilication. It was established that the use of phosphoric acid as an activating agent contributes to the development of N_2 -BET surface area of the synthesized products up to $1690 \text{ m}^2/\text{g}$; while according to linear Langmuir-isotherm model, the maximal MB adsorption capacity reaches 667 mg/g . It is suggested that carbon materials with a given surface area, given pore size distribution and volume may be obtained by varying the activation conditions for rice husk. It was shown that the acid to precursor ratio within range of 1.5 to 2 for temperature interval of $400\text{--}500^\circ\text{C}$ is optimal for maximization of the specific surface area, porosity and sorption capacity of the resulting carbon materials towards basic dye molecules of methylene blue. Low-temperature N_2 -adsorption together with methylene blue adsorption studies results, as well as SEM-investigation of the samples revealed both high specific surface area and mesoporosity of the activated carbons obtained within temperature range of $300\text{--}600^\circ\text{C}$ at impregnation ratio of 2, making them suitable to be employed in catalytic, adsorption and electrochemical processes, e.g.: as a Rh-catalyst support for hydrogenation of aromatic hydrocarbons, in hemosorbents preparation, as electrode material for Li-ion batteries, etc. Elemental analyses of these carbons suggested sufficient degree of carbonization and functionalization of their surface with acidic phosphate functional groups.

Acknowledgments

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