Mesoporous Composite Materials from Acivated Rice husk Carbon and Montmorillonite

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Abstract

Three different carbons were prepared from rice husk by steam activation at 700 ºC, H_3PO_4-activation followed by desilication or desilication followed by H_3PO_4-activation at 500ºC. Honeycomb monoliths were obtained by mixing of a carbon with montmorillonite followed by extrusion, curing, calcination and leaching by alkaline solution. Obtained blocks were compared in terms of their morphology and elemental composition using data of SEM/EDX-analysis. From low temperature nitrogen adsorption study results it follows that prepared monoliths are characterized by SBET up to 700 m^2/g (V_Σ = 0.79 cm^3/g) and pore size distribution shows the maximum around 4 nm. Methylene blue number is as high as 250 mg/g.

Introduction

Lignocellulosic materials, *e.g.*: vegetable wastes are renewable and inexhaustible source of carbons, provided that the development of suitable methods for the production of these carbons is sustainable. Besides, they have a more even geographic distribution compared to that of coal or oil. Thus, lignocellulosic materials are recyclable natural resources that are technically feasible alternative to fossil fuel in the production of carbon materials.

Rice husk (RH) is a large-scale (up to 600 mn ton per annum) agricultural waste and various methods of its activation to produce carbon materials are well described and reported. Activated carbons (AC) with specific surface area up to 273 m^2/g were obtained from RH using single-stage steam activation or carbonization in inert atmosphere [1, 2], AC with specific surface area up to 3000 and 2500 m^2/g were obtained from RH by chemical activation using KOH and NaOH [3, 4] respectively.

AC obtained from RH via H_3PO_4-activation, were studied for the removal efficiency of various pollutants [5-7], but there was limited information about the properties of these AC. Highly mesoporous carbons with relatively low values of specific surface area and total pore volume were obtained from RH by a two-stage process (precarbonization with subsequent activation by H_3PO_4 in the temperature range 700-900 °C) [8]. AC with a specific surface area and total pore volume of up to 874 m^2/g and 0.713 cm^3/g, respectively, were obtained from RH through the activation using H_3PO_4 [9]. Analysis of the publications showed that the high ash content of the AC obtained from RH via H_3PO_4-activation, which lies within the range of 20-70% and is associated with the presence of silica [5, 7, 9], prevents these AC industrial production and application.

In this study the attempt was made to obtain such carbon materials in which a prospect of additional pore development is realized through base leaching of silica or otherwise called "desilication procedure" applied to either starting RH or carbonized RH (CRH) either before and/or after honeycomb monoliths preparation using alkaline aqueous solution under mild conditions.

We have reported of such techniques regarding RH-carbonized materials in our previous publications [10-11], but this time the materials of both high added value and larger specific surface area with predominantly mesoporous structure were obtained for specific purposes.

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Experimental

Synthesis of carbonized rice husk materials

Rice husk carbonization in steam atmosphere

RH pyrolysis was carried out at 700 ºC attained at a ramp rate of 2.5 ºC /min and additional steam activation for 90 min thereafter was fulfilled. For such carbonization technique, 500 cm^3 of RH was loaded into a rotary steel reactor placed in an electrically heated furnace and equipped with capillary injection system. Liquid water volume rate was maintained at 100 cm^3/h.

H_3PO_4 activation of rice husk

70% phosphoric acid ($\rho \approx 1.54$ g/cm^3) was admixed to the appropriate amount of RH or desilicated RH (see the procedure 1.4 below) to make H_3PO_4/precursor (wt/wt) impregnation ratio of 2:1. The mixtures were transferred into alumina crucibles, precarbonized in an oven at 200 ºC for 12 hours, loosely covered with stoppers and activated at 500 °C during 1 hour in a vertical cylindrical furnace equipped with chromel/alumel thermocouple at the temperature ramp rate of ca. 5 ºC /min. CRH were continuously washed with hot distilled water till neutral pH.

Preparation of honeycomb monoliths using carbonized rice husk and montmorillonite

For monoliths preparation we used Ca-montmorillonite (as a binder) and three different carbons prepared from rice husk by: steam activation at 700 ºC, H_3PO_4-activation followed by desilication or desilication followed by H_3PO_4-activation at 500 ºC. CRH was grinded into powder with particle size of ca. 50-100 mm. Ca-M was dispersed in water under intense stirring with electric stirrer to obtain a homogeneous suspension. The suspension was poured into a flat vessel and allowed to stay open for several days until the clay swelled and a viscous mass with the moisture content 65–68% formed. The CRH powder and Ca-M suspension were blended in a Z-shape mixer for 15–30 min. The optimal ratios of CRH to Ca-M necessary to obtain a plastic mass are 3:2 for CRH-700 and 1:1 in case of H_3PO_4-activated CRH. Moisture content of the mass ready for molding is 45–50%. First, the mass was consolidated and compacted by vacuum, then extruded through a die plate 10 mm in diameter using a pneumatic press with a vertical piston. This was followed by drying, which is an essential preparation step. Moisture transfer and shrinkage proceeding in a wet monolith have impact on the finished product shaping (bending, channels rupture, and cracking) and mechanical strength. Thus, the formed monoliths were first seasoned for 3 days in cartons permeable to water vapor, then dried at 100 ºC, and calcined at 700 ºC in flowing Ar. The chosen calcination temperature provides very high water resistance of monoliths at mild conditions.

Chemical treatment with alkaline agents

For initial rice husk desilication to finally obtain CRH-P-500 B/A, 300 g of RH was placed into a 5L Pyrex glass beaker and filled with 3L of aqueous 2M NaOH. Mixture was boiled on a hotplate for half-hour, the solute was decanted, desilicated RH was washed by a multistep technique using boiling-sedimentation-decantation procedures.

To obtain CRH-P-500, the carbonaceous residue upon H_3PO_4 activation underwent additional desilication in 0.5M NaOH and washing with hot distilled water till neutral pH. Samples were dried in hot air oven at 110±5 °C

The finished monoliths made of CRH were treated with a 12% solution of NaOH or KOH at 70-80 °C for 3 h. The volume ratio of liquid and solid was 10:1. After treatment in alkaline solution, samples were washed out repeatedly with a large amount of distilled water to remove soluble silicate compounds. The steps of alkaline treatment and washing with water were repeated a few times. Then the monoliths were blown by air to remove moisture from the channels and dried at 100 °C for 2 h.

Physical methods of investigation

Thermal desorption of argon and Low-temperature nitrogen adsorption

Specific surface area of the samples were determined by argon thermal desorption using analyzer SORBI N.4.1. Information on microporous & 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 & residual pressure of 0.001 mm Hg. The measurements of were conducted at 77 °K within range of relative pressures from 0.005 to 0.991.

Adsorption of methylene blue

Methylene blue was dissolved in distilled water to prepare the stock solution (1.50 g/L). Calibration solutions of desired concentration for spectrophotometric evaluation were obtained by successive dilution. Twenty-five milliliters of dye solution was added to 0.10 g activated carbon in a 50 mL glass-stoppered flask on a magnetic stirrer at room temperature for 20 min. Then the absorbance of supernatant solution was estimated to determine the residual concentration to calculate the methylene blue (MB) number.

Scanning electron microscopy

The morphology of activated carbons was studied by scanning electron microscopy (SEM) using a QUANTA 3D 200i microscope (FEI, USA) with accelerating voltage of 30 kV equipped with EDAX analyzer for local chemical (semiquantitative) analysis.

Results and discussion

In the Laboratory, Environmental Catalysis at Boreskov Institute of Catalysis, SB RAS (Novosibirsk), we obtained blocks of cellular structure based of CRH and a binder Ca-M-montmorillonite of the following composition: $Ca_{0.2}(Al,Mg)_2Si_4O_{10}(OH)_2{}^{\times}4H_2O$.

Physico-chemical principles of porous structure formation and properties of blocks of cellular structure during extrusion, calcination and activation are similar to those of established for other CRH-based molding compositions previously described [10-11] .

Scheme of preparation of blocks of cellular structure of carbon materials obtained by carbonization of rice husk and their physico-chemical parameters including textural properties according to adsorption studies and carbon content according to EDAX analyzer data is shown in Figure 1 and Table1.

As we formerly mentioned, for additional pore space formation in the blocks, a desilication technique was employed using NaOH basic solution to remove silica in form of sodium silicates.

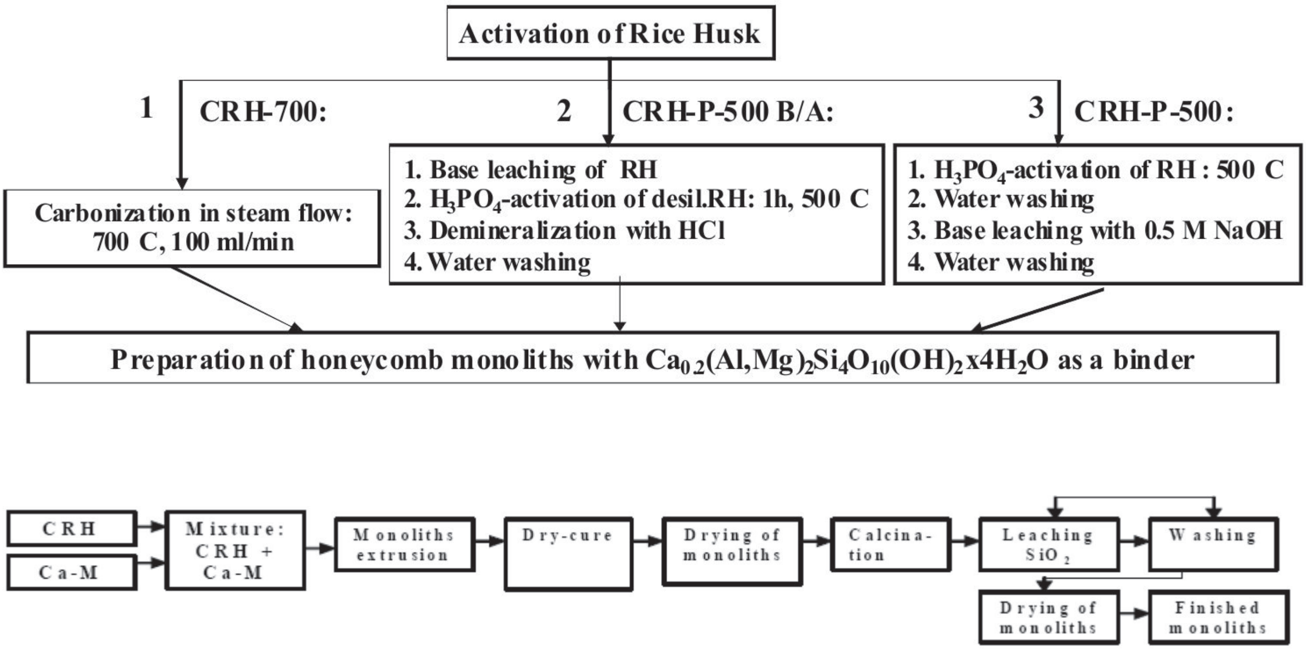

Fig.1 Schemes of CRH syntheses and honeycomb monoliths design

Table 1.

Approximate carbon content and textural properties of CRH samples and the corresponding blocks according to argon, nitrogen and methylene blue adsorption studies

#	Sample	C,%	SBET Ar m^2/g	SBET N_2 m^2/g	V_Σ (V_μ) cm^3/g	MB number, mg/g
	CRH-700		262	220	0.14 (0.1)	
1a	block 1a (60% CRH-700+40% Ca-M) before leaching			167	0,14	
1b	block 1b (60% CRH-700+40% Ca-M) after leaching	42.47	325	310	0.32	97
	CRH-P-500 B/A		1800	1300	1.62	
2a	block 2a (50% CRH-P-500 B/A +50% Ca-M) before leaching		729	584	0.73	
2b	block 2b (50% CRH-P-500 B/A +50% Ca-M) after leaching	65.94	835	700	0.79	250
3a	block 3a (50% CRH-P-500 +50% Ca-M) before leaching			548	0.52	
3b	block 3b (50% CRH-P-500 +50% Ca-M) after leaching	60.20	856	628	0.51	245

It can be seen from Table 1 that both MB-number and the pore volume, as well as the specific surface area of the blocks corresponds to the fraction of carbon material in the molding composition.

Differential pore size distribution in the starting materials, *e.g.*: CRH-700, CRH-P-500 B/A, CRH-P-500 and in the corresponding blocks before and after desilication are presented in Figures 2-4. Differential pore size distributions shown on Figure 2 for siliceous starting material CRH-700 and the block (1a) before leaching are nearly the same. Leaching of silica from the block (1a) leads to a significant development of porous space of the block 1b (Fig. 2, curve-1b).

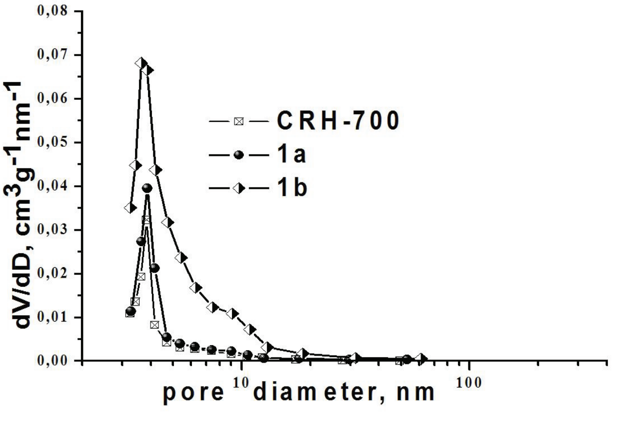

Fig. 2. Differential pore size distribution in the starting material CRH-700 and in corresponding blocks: 1a- before leaching, 1b- after leaching.

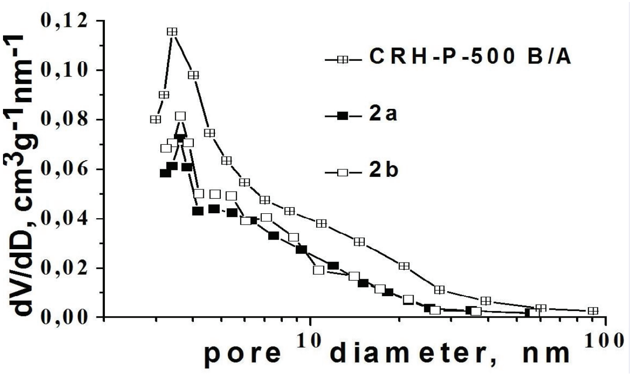

Fig. 3. Differential pore size distribution in the starting material CRH-P-500 B/A and in corresponding blocks: 2a- before leaching, 2b- after leaching.

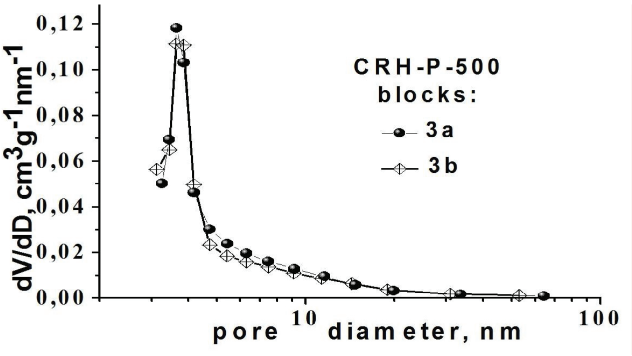

Fig. 4. Differential pore size distribution in the blocks based on CRH-P-500: 3a - before leaching, 3b - after leaching.

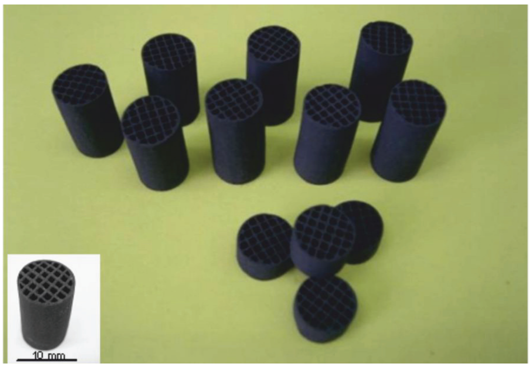

Fig. 5. External appearance of the CRH- honeycomb monoliths.

Starting material CRH-P-500 B/A (Fig. 3) was subjected to SiO_2-leaching during the synthesis, so upon the comparison of its differential pore size distribution curve to the corresponding curves for the blocks obtained one can observe a significant decrease in pore volume (Fig. 3, curve-2a and 2b).

Leaching of SiO_2 from the blocks leads to a significant improvement of textural parameters only if siliceous CRH 700 is used as a starting material. In case of desilicated CRH (CRH-P-500 and CRH-P-500 B/A), leaching of SiO_2 occurs from montmorillonite and textural parameters change insignificantly: see Figure 3 and 4 and compare the corresponding curves 2a, 2b and 3a, 3b with one another within each set; also compare pore volumes of the corresponding blocks shown in Table 1 accordingly.

Photographs of the CRH-based blocks are shown in Figure 5.

CRH-based honeycomb monoliths prepared as described above, have the composition of 60% CRH + 40% Ca-M (by mass) in the case of CRH obtained by carbonization and/or steam activation of the initial RH. The use of phosphoric acid as an activating agent during RH carbonization yielded carbon nanomaterials suitable for molding of honeycomb structure already at a weight ratio of CRH to binder Ca-M - 1:1 or (50% +50%). Reduction of the mass fraction of binder (Ca-M) with a low specific surface area (50 m^2/g), allows to increase the surface area of the obtained blocks.

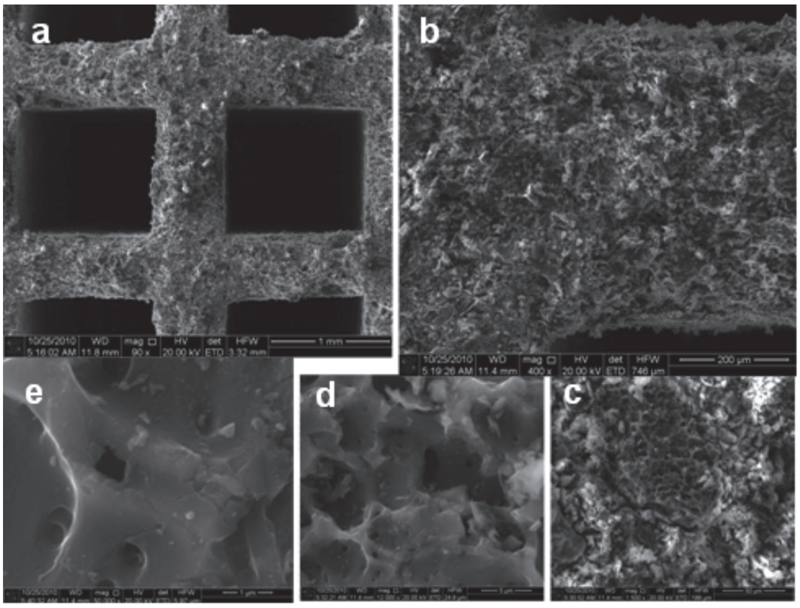

Fig. 5. External appearance of the CRH- honeycomb monoliths.

SEM images of the honeycomb monoliths prepared from CRH-700, CRH-P-500 B/A and CRH-P-500 are shown in Figs 6, 8 and 10 respectively, corresponding energy dispersion microanalyses (EDAX) are shown in Figs 7, 9 and 11 and the data are summarized in Tables 2-4 respectively.

SEM images of cross-sections of monoliths and monolith material at high magnification demonstrate that morphological properties of the material are determined by the morphology of monolith components, fragments of CRH and Ca-M. EDAX analyses show the presence of alumosilicate (Ca-M) components.

Table 2.

Elemental composition of the block 1b

Element	C	O	Mg	Al	Si	K	Ca	Fe
%	42.47	30.81	1.09	4.80	17.94	0.40	1.26	1.23

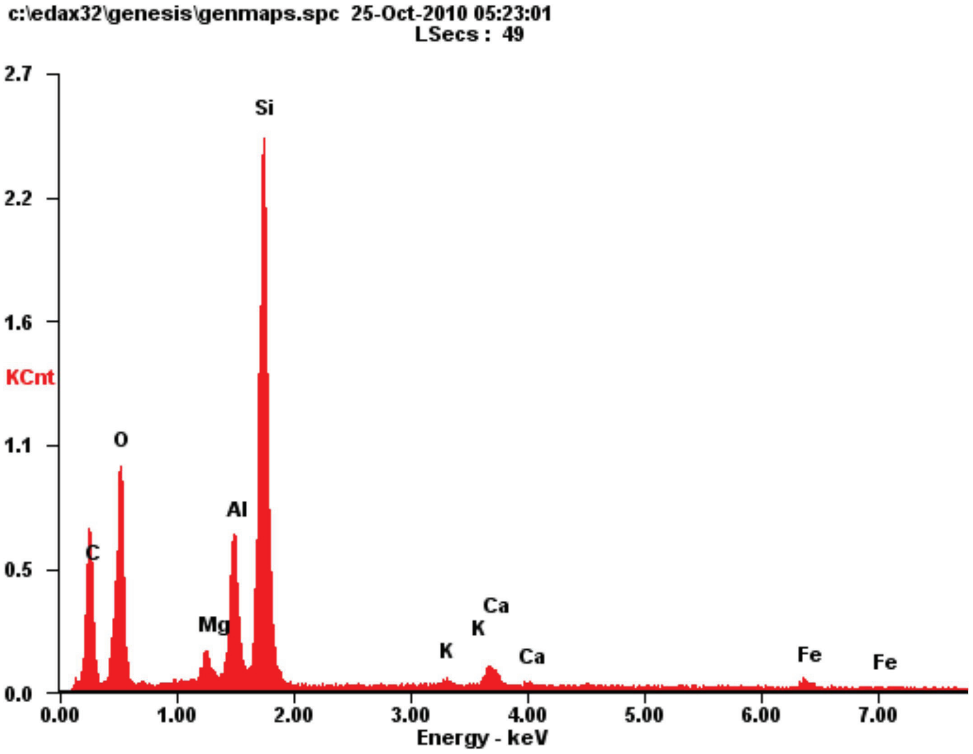

Fig. 7. EDAX elemental microanalysis of block 1b.

Table 3.

Elemental composition of the block 2b

Element	C	O	Na	Mg	Al	Si	P	Ca	Fe
%	65.94	18.17	0.14	0.91	4.09	8.83	0.30	0.70	0.94

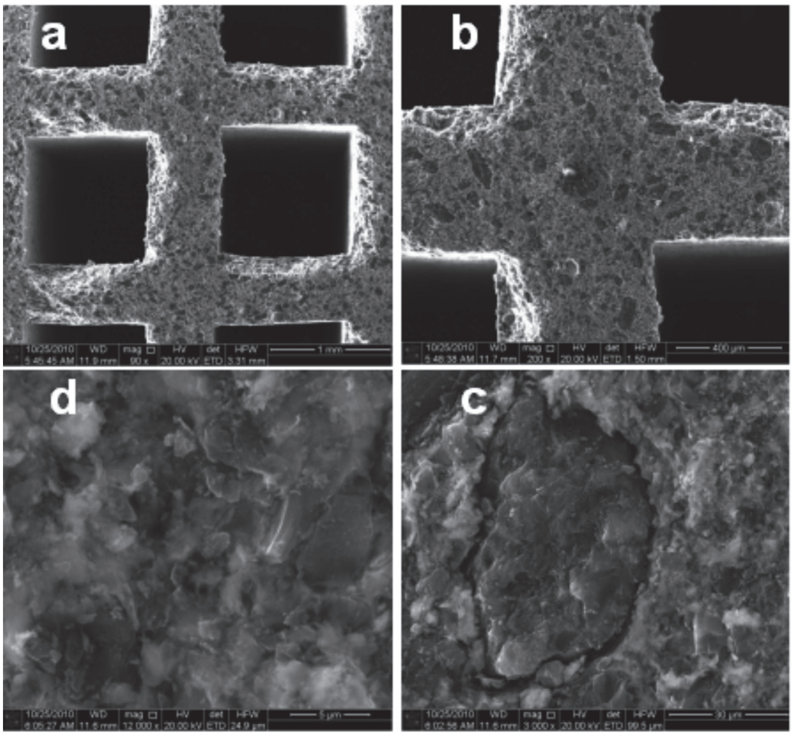

Fig. 8. SEM images of the block 2b with magnification of for: a - x 90; b- x 200; c- x 3 000; d- x 12 000

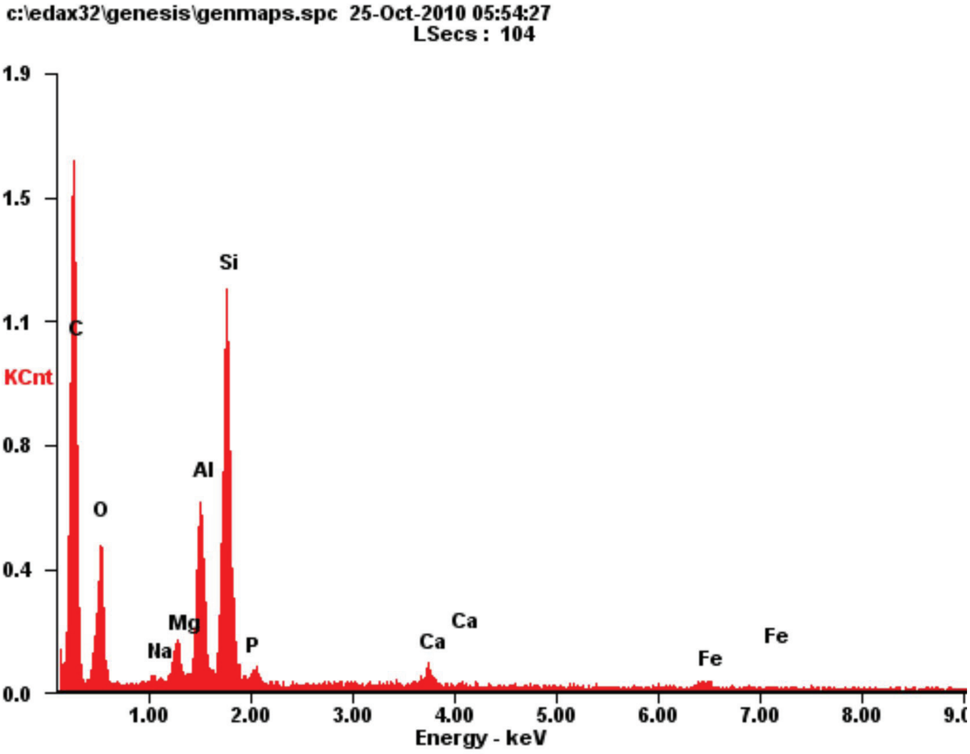

Fig. 9. EDAX elemental microanalysis of block 2b

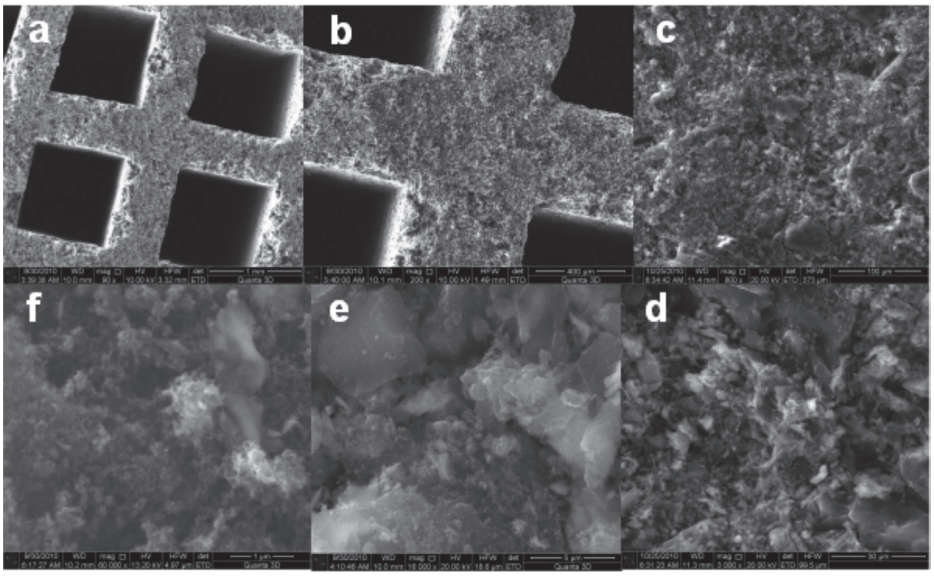

Fig. 10. SEM images of the block 3b with magnification of for:
a- x 90; b- x 200; c- x 800; d- x 3 000; e- x 16 000; f- x 60 000

Table 4.
Elemental composition of the block #3

Element	C	O	Mg	Al	Si	K	Ca	Fe
%	60.20	21.74	1.00	4.84	9.92	0.29	0.83	1.18

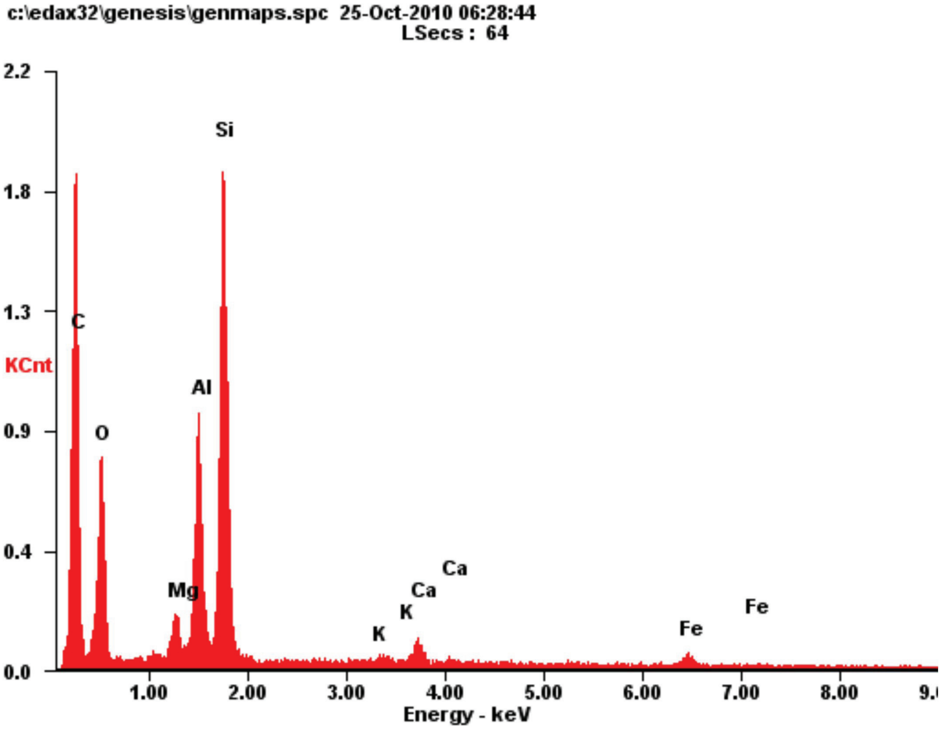

Fig. 11. EDAX elemental microanalysis of block 3b

Conclusion

Three different rice husk based carbons were obtained and used for honeycomb monoliths preparation using different physical and chemical activation techniques including carbonization in presence of phosphoric acid and desilication using caustic soda solution. From nitrogen adsorption data and BJH-pore size distribution it follows that mesoporous materials with large pore volume were obtained. The porosity of such materials depending on the needs can be controlled by varying the activation conditions. These properties are appropriate for further use of the monoliths as catalyst supports and adsorbents.

References

1. Alaya M.N., Girgis B.S., Mourad W.E. Activated carbon from some agricultural wastes under action of one-step steam pyrolysis // Journal of Porous Materials.- 2002.- № 7.- P.509.
2. Mansurov Z.A., Zhylybaeva N.K., Ualieva P.S. and Mansurova R.M. Obtaining procedure and properties of the sorbents from plant raw material // Chemistry for Sustainable Development. -2002. –Vol. 10. - P. 321-328.
3. Guo Y., Yang S., Yu K., Zhao J., Wang Z., Xu H. Carbon materials for advanced //Materials Chemistry and Physics.- 2002.- № 74.- P. 320.
4. Guo Y., Yu K., Wang Z., Xu H. Effects of activation conditions on preparation of porous carbon from rice husk // Carbon.- 2003.- № 41.- P.1645.
5. Daifullah A.A.M., Girgis B.S., Gad H.M.H. Colloids and Surfaces A// Physico-chemical and Engineering Aspects.- 2004.- № 235.- P.1.
6. Mohamed M.M. Acid dye removal: comparison of surfactant-modified mesoporous FSM-16 with activated carbon derived from rice husk // Journal of Colloid and Interface Science.- 2004.- № 272.-P. 28.
7. Rahman I.A., Saad B., Shaidan B., Sya Rizal E.S. Adsorption Characteristics Of Malachite Green On Activated Carbon Derived From Rice Husks Produced By Chemical-Thermal Process // Bioresource Technology.- 2005.- № 96.- P. 1578.
8. Kennedy L.J., Vijaya J.J., Sekaran G. Effect of two stage process on the preparation and characterization of porous carbon composite from rice husk by phosphoric acid activation // Industrial & Engineering Chemistry Research.- 2004.- № 43.- P.1832.
9. Khalil L.B. //Adsorption Science & Technology.- 1996.- № 14.- P.317.
10. Ismagilov, Zinfer R., Shikina, Nadezhda V., Andrievskaya, Irina P., Rudina, Nina A., Mansurov, Zulkhair A., Burkitbaev, Mukash M.,. Preparation of carbonized rice husk monoliths and modification of the porous structure by SiO2 leaching. Catalysis Today, (2009), V.147, № 3-4, pp.58-65
11. Jandosov J.M., Shikina N.V., Bijsenbayev M.A., Shamalov M.E., Ismagilov Z.R., Mansurov Z.A. Evaluation of Synthetic Conditions for H3PO4 Chemically Activated Rice Husk and Preparation of Honeycomb Monoliths // Eurasian Chemico-technological Journal. – 2009. - №3. - pp. 245-253.

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