Bulgarian Chemical Communications, Volume 42, Number 2 (pp. 130–137) 2010

Preparation of low-ash-content porous carbonaceous material from rice husks

S. A. Uzunova[1]*, I. M. Uzunov[2], S. V. Vassilev[3], A. K. Alexandrova[3],
S. G. Staykov[1], D. B. Angelova[1]

[1] *University of Chemical Technology and Metallurgy, 8 Kliment Ohridski Blv., 1756 Sofia; Bulgaria*
[2] *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences,*
Acad. G. Bonchev St., Block 11, 1113 Sofia, Bulgaria
[3] *Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences,*
Acad. G. Bonchev St., Block 10, 1113 Sofia, Bulgaria

Received May 22, 2009; Revised December 18, 2009

The effect of preliminary removal of silica from raw material was studied as well as that of the use of a new activating agent (carbamide) on the properties of porous carbonaceous material, obtained by chemical activation of rice husks. Two different approaches have been applied to prepare the porous carbonaceous material of low-ash content below 1% and specific surface area above 1000 $m^2 \cdot g^{-1}$. The first one consists in pyrolysis of rice husks at 450ºC with consecutive removal of silica with hydrofluoric acid and chemical activation at 700ºC (series of samples 1S). The second approach consists in removal of silica from the raw material – rice husks with a consecutive intermediate step of pyrolysis at 450ºC and chemical activation at 700ºC (series of samples 2S). Carbamide, NaOH and $ZnCl_2$ have been used as activating agents.

It was established that the sequence of treatment of the rice husks influences the value of the specific surface area of the two precursors: 495 $m^2 \cdot g^{-1}$ (for the series 1S) and 105 $m^2 \cdot g^{-1}$ (for the series 2S) and the specific surface area of the final product depends on the kind of the applied activating agent. The samples of carbonaceous material activated using carbamide possess specific surface areas of 1259 $m^2 \cdot g^{-1}$ and 1229 $m^2 \cdot g^{-1}$, respectively, ash contents – 0.88% and 1.5%, iodine adsorption capacity – 1133 $mgJ_2 \cdot g^{-1}$ and 983 $mgJ_2 \cdot g^{-1}$ and total pore volumes 0.81 $cm^3 \cdot g^{-1}$ and 0.70 $cm^3 \cdot g^{-1}$.

Due to their high specific surface areas and low ash contents the carbonaceous materials, prepared by us, can be investigated as adsorbents, catalyst supports, active materials for electrochemical power sources, including in super capacitors and etc.

Key words: porous carbon; rice husk; activation; carbamide; surface area

INTRODUCTION

Among the adsorption materials, porous carbons can be widely used as industrial adsorbents for separation, purification, and recovery processes due to their large surface area and porosity [1–3]. Recent applications using porous carbons as an electrode material for electric double layer capacitors or supercapacitors have inspired intensive research work worldwide focused on their porous structures and electrochemical behaviour [4–7]. Various carbon-containing raw materials have been used to prepare active carbons. Special attention is paid to the processing of agricultural wastes to active carbon materials [8–10].

Several series of hard carbons, used as anodes of lithium-ion batteries, have been prepared by pyrolysis of natural or agricultural precursors such as sugar [11–13], cotton [14] and coffee beans [15]. Among these, the rice husks occupy a special position, due to their high ash content. The composition of the rice husks depends on the kind of agrotechnical activities, the soil and the climatic conditions, in the region where the rice is grown. The chemical analyses indicate that rice husks consist of lignin, cellulose and hemi cellulose. The latter is a mixture of D-xylose, L-arabinose, methylglucoronic acid and D-galactose. What is characteristic of rice is the fact that its metabolism is connected with extraction from the soil and accumulation of amorphous SiO_2, mainly in the external epidermis layer of the rice husk. Its content varies from 15 up to 22% [16, 17].

Rice husk is a by-product of the rice milling industry and it accounts for about 20% of the whole rice grain. The amount of rice husk was estimated to be approximately 500 millions of tons in developing countries [18]. In Bulgaria, the annual production of rice exceeds 28000 tons. The processing of this renewable waste into products valuable for the practice will have a double sided effect – both for the economy and for the ecology.

The initial raw material for preparing carbonaceous material in the present work was rice husks from the Pazardzhik region (harvested in 2008). The

---

* To whom all correspondence should be sent:
E-mail: snejanka.uzunova@gmail.com

basic requirements to active carbon materials used in electrochemical power sources, including lithium-ion accumulators and super-capacitors, are the high specific surface area, low ash content and optimum porosity [19, 20]. It is known that the specific surface area, the porosity and the ash content in the active carbon material depend on the composition and properties of the precursor materials and on the method of activation. Two general methods are used for the preparation of activated carbon [21, 22]. The first one, the physical activation, consists in heating at a high temperature in the presence of a charcoal gasification reactant (H_2O or CO_2). The other method, chemical activation, consists of heating at a relatively lower temperature with the addition of a dehydration agent (e.g., H_3PO_4, $ZnCl_2$). Nowadays, there is a great interest in the alkali hydroxide activation process for the production of activated carbons [23]. The application of these activating agents to the preparation of carbon materials from rice husks leads to the obtaining of final products having high ash content, which is connected both with the chemistry of the process of activation and with the high ash content of the rice husks [24, 25]. Most of the authors, who have published results of their studies on the preparation of carbon materials of high specific surface area from rice husks, do not discuss the problem of the ash content in the raw material and in the final product [26]. Some of the authors have shown that micro quantities of silica in the carbon material influence favourably in case of using it into electrochemical power sources [27, 28].

With purpose to prepare a low ash content porous carbonaceous material, we removed in advance the main inorganic component of the rice husk composition. The removal of silica was carried out by treatment with hydrofluoric acid. The aim of the present work was to obtain porous carbon material with optimal characteristics (high specific surface area and low ash content) using two different approaches for processing of the rice husks and various activating agents. The first approach consists in the removal of silica from the rice husks pyrolysed in advance, followed by the consecutive step of chemical activation (series of samples 1S). The second approach is based on removal of silica from the raw rice husks and consecutive steps of intermediate pyrolysis and chemical activation (series of samples 2S). The effect of the activating action of carbamide was studied and compared to that of some of the most frequently applied substances for preparing porous carbon by chemical activation – NaOH and $ZnCl_2$ [19, 23].

EXPERIMENTAL

In order to eliminate mechanical admixtures the rice husks were washed several times with hot water and dried at 110ºC for 2 hours. The intermediate pyrolysis of the rice husks is carried out in a reactor at 450ºC. The temperature of the furnace was increased linearly from room temperature up to the value needed for pyrolysis at a heating rate of 4 $deg \cdot min^{-1}$ and temperature retention for 3 hours. The time interval, within which the temperature was maintained constant, is defined as “time of pyrolysis”. The sample was taken out after cooling first the oven down to room temperature (samples 1S1 and 2S2).

The removal of SiO_2 was accomplished by treatment of the rice husks with 40% HF acid and washing with deionized water to reach pH 6.5 (samples 1S2 and 2S1). The process of activation was carried out by preliminary treatment of the precursors 1S2 and 2S2 with the activating agent at a ratio C:activator equal to 1:5 for $(NH_2)_2CO$ and $ZnCl_2$ and 1:4 for NaOH. The samples, prepared in this way, were carbonized in the absence of air at a temperature of 700ºC in the course of 1 hour.

The samples 1S3 and 2S3 were obtained using activator urea, the samples 1S4 and 2S4 – with activator NaOH and the samples 1S5 and 2S5 with activator $ZnCl_2$. After cooling the samples 1S4 and 2S4 were washed with hot deionized water to reach pH 6.5 and then dried at 110ºC. Aiming at removal of the ash residual the samples 1S5 and 2S5 were treated with hydrochloric acid (1:1) in hot state, upon refluxing for 1 hour. After removal of the acid, the samples were washed with hot deionized water to reach pH 6.5 and dried at 110ºC.

The phase composition was determined by a Philips ADP 15 diffractometer using CuK_α radiation. The infrared spectra were recorded on a Nicolet-320 FTIR spectrometer in a tablet of KBr. The measurement of the specific surface area by the BET method was carried out on an Area Meter, Strolein apparatus. The porous structure of the samples was measured by mercury intrusion porosimetry. The measurements were perfomed with an apparatus AutoPore 9200, MICROMERITICS. The thermal analysis was carried out on a SETARAM *Labsys Evo* apparatus in a corundum crucible at a heating rate of 10 $deg \cdot min^{-1}$ in air medium.

Carbon and hydrogen amounts in raw rise husks were determined by the so-called high-speed method of analysis. The method consists in burning of the sample into an oxygen flow. The semi-quantitative atomic emission spectral analysis with excitation in direct current arch was accomplished on a spectrograph PGS, Germany. The admixtures of alkali elements and iron in the rice husks were determined by flame atomic absorption spectrometer SOLAR M5, Thermo. The ash content in the carbon materials was determined based on the Bulgarian standard method [29]. The iodine adsorption capacity was determined by titration of the residual solution of 10 ml with 0.1 N $Na_2S_2O_3$ in the presence of 1 ml of 1% starch solution as an indicator. The iodine adsorption capacity was determined based on the adsorbed iodine per mass unit of the adsorbent at the residual iodine concentration of 0.02 N [30].

RESULTS AND DISCUSSION

The complex thermal analysis (DTA, TG) Fig. 1 reveals the occurrence of an endothermal process up to 120ºC, connected with the liberation of moisture from the rice husks, amounting to 5%. The exothermal process, which takes place within the interval 260–493ºC, is characterized by a maximum at 348ºC, which is associated with thermal degradation of the organic components included in the the rice husks and transformation of the lignin cellulose material into carbon. There follows combustion of the carbon residue and this process is reflected in the curve by a maximum аш 454ºC.

The ash content in the carbon material depends on the quantity of inorganic admixtures in the initial raw material and on the way of activation of the material. The quantity of ash in the rice husks, used by us, amounts to 21% and as it can be seen from the data listed below, the ash contains also some other inorganic substances, in addition to the silica. The organic elemental analysis carried out reveals composition of the rice husks as shown on Table 1. According to these data, the organic component in the rice husks amounts to about 79%.

The semi-quantitative composition of the initial raw material was determined by emission spectral analysis (Table 2a). The quantity of the admixtures of sodium, potassium and iron in the rice husks was evaluated by atomic absorption analysis (Table 2b). The specific surface area of the raw rice husks, determined by the B.E.T. method is about 4 $m^2 \cdot g^{-1}$.

Figures 2a and 2b represent the data of the IR-spectroscopy analysis of the raw rice husks and the series of samples 1S (a) and 2S (b). The observed absorption bands in the spectrum of the 2S1 (Fig. 2b) reflect the changes, occurring in the phase composition of the rice husks as a consequence of their treatment with HF acid. Although it is a weak acid, the hydrofluoric acid causes partial hydrolysis of the lignin-cellulose material, building up the rice husks. In parallel to this process, the acid interacts actively with the silica, whose amount in the rice husks, used by us, amounts to 21%.

Table 1. Elemental organic analysis of raw rice husks.

Sample, mg	H_2O, mg	CO_2, mg	H, %	C, %	Residue, mg
5.980	2.350	8.600	4.305	38.400	1.270

Table 2a. Amount of some metallic ingredients as oxides in raw rice husk.

Ca, $\mu g \cdot g^{-1}$	Mn, $\mu g \cdot g^{-1}$	Mg, $\mu g \cdot g^{-1}$	Zn, $\mu g \cdot g^{-1}$	Cu, $\mu g \cdot g^{-1}$
$< 1 \times 10^2$	$n \times 10^1$	$n \times 10^1$	$< 1 \times 10^1$	$\sim 1 \times 10^1$

Table 2b. Amount of alkali and iron in raw rice husk.

Element	Quantity, $\mu g \cdot g^{-1}$
Na	370 ± 10
K	580 ± 10
Fe	330 ± 10

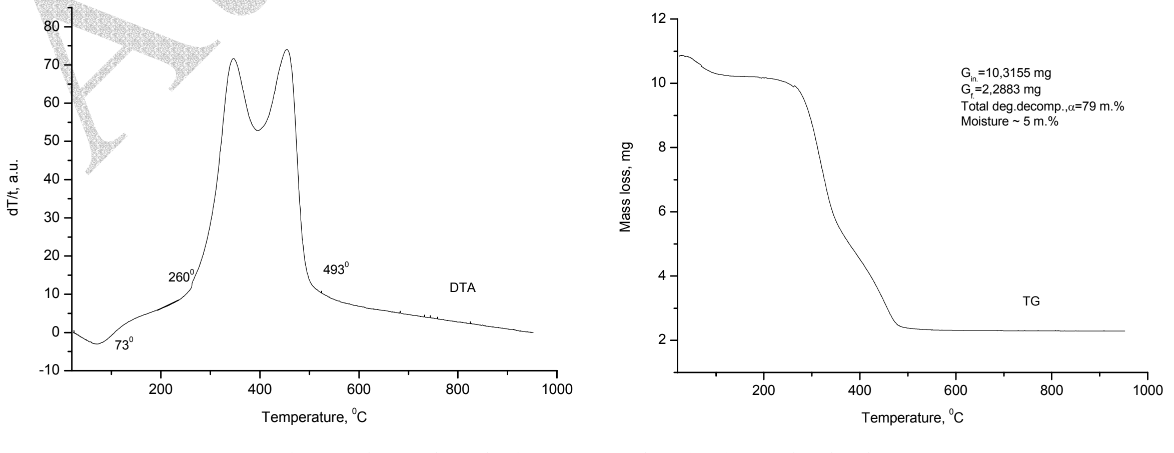

Fig. 1. Thermal analysis (DTA and TG) of raw rice husks.

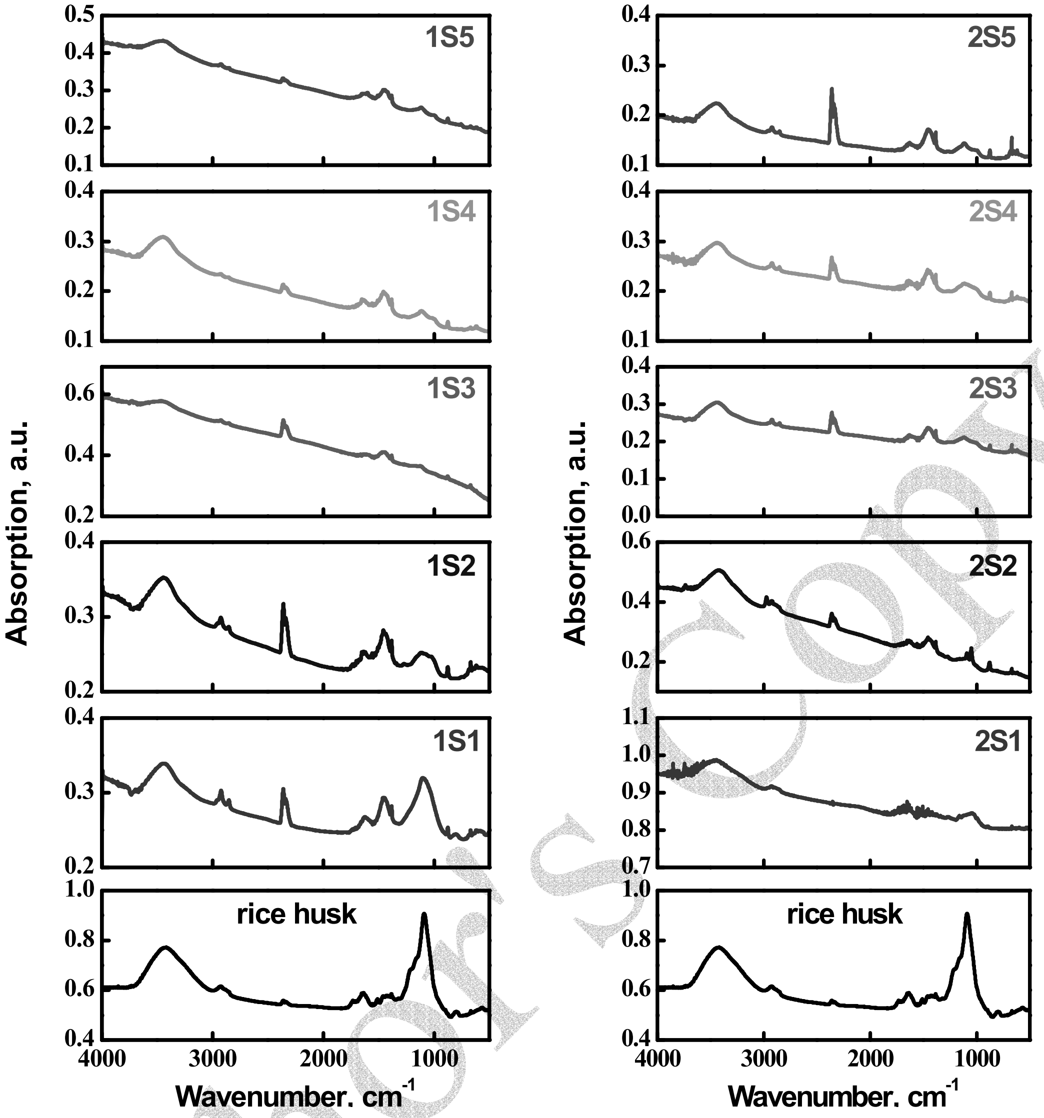

Fig. 2a, b. IR absorption spectra of raw rice husks (RH) and series of samples 1S (a) and 2S (b).

The bands in the interval 1350–1480 cm^{-1} can be attributed to be specific features, connected with the hydrocarbon structure of the rice husks. The absorption bands at 1733 and 1635 cm^{-1}, as well as the one at 1512 cm^{-1}, are due to stretching vibrations of the double bond C=O in the structure of the lignin-cellulose material. The absorption at 1425 and 1454 cm^{-1} is connected with bending vibrations of the bond C=O in the carboxylic groups, which depend on the presence of a metallic ion in the compound.

The presence of hydrated SiO_2 in the structure of the rice husks is proved by the bands in the low wavelength region of the spectrum (470–790 cm^{-1}), as well as by the intensive band at 1089 cm^{-1} with shoulders at 1159 and 1208 cm^{-1}. These are bands, typical of the two low-temperature forms of SiO_2 – tridymite and crystobalite [31].

The extraction of SiO_2 as a result of its interaction with HF acid leads to change in the IR-spectrum of the rice husks. This fact can be explained by partial hydrolysis of the lignin-cellulose material, as well as by processes of destruction, associated with the extraction of biogenic SiO_2. Its reaction with HF leads to disruption of its bonds with monosaccharides included in the composition of the rice husks. The basic bands of the two modifications of silica are missing in the spectrum of the acid treated material. The evidence for the SiO_2 still present in the structure of ash-purified material are the bands at 1038 cm^{-1}, attributed to elastic vibrations of the bond Si–O–C [32, 33], the one at 1456 cm^{-1}, due to vibrations of the bond C=O in the carboxyl groups, depending on the presence of Si, as well as the band at 1158 cm^{-1}, connected with the asymmetric vibrations of the siloxane bond Si–O–Si. In the spectrum of the rice husks, treated with hydrofluoric acid, there appears a new absorption band at 895 cm^{-1}, associated with, as well as the wide band at 1652 cm^{-1}, with stretching mode of the bonds C–O–H and C=O of the acid-hydrolysed hydrocarbon composition of the material. The weak band at 1271 cm^{-1} is also connected with the C=O bond vibrations. The wide band with a maximum at 2924 cm^{-1} and a shoulder at 2867 cm^{-1}, which are present also in the spectrum of the raw rice husks, are connected with the methyl groups included in the composition of the husks. The hydroxyl groups of the structure of polysaccharides and lignin, as well as those of the chemisorbed water, are associated with the wide band at 3445 cm^{-1}.

The pyrolysis of the sample 2S1 implies thermal destruction of a large part of the lignin-cellulose material, which results in increase of the concentration of the SiO_2 remaining in the structure of the rice husks. As a consequence of this, there appear bands in the low wavelength region of the IR-spectrum, which are characteristic of crystobalite. The shape of the wide band in the region 1000–1200 cm^{-1} is changed. Among the group of bands, characteristic of the raw rice husks, again the one at 1383 cm^{-1} appears, connected with the presence of $-CH_3$ groups. The presence of $-CH_2$ and $-CH_3$ groups in the composition of pyrolysed material is associated with the band at 1449 cm^{-1}. Other absorption bands are also observed, characteristic of the acid-treated material.

The comparison of the spectra of the activated products with the spectrum of the precursor (2S2) shows that whatever the kind of the activating agent is and in spite of the increase of the temperature of calcination no changes occur in the phase composition of the material. This shows that the preliminary pyrolysis of the rice husks at 450ºC involves the building of a stable phase structure. The application of activating agents leads only to change in the value of the specific surface area and in the porous structure of the carbonaceous material.

The thermal destruction of rice husks at 450ºC (sample 1S1, Fig. 2a) leads to change in the phase composition of the material. The group of bands in the interval 1350–1730 cm^{-1} characteristic of the raw rice husks disappears. Other absorption bands appear having maxima at 1383, 1454 и 1626 cm^{-1}. The strongest band in the spectrum of raw rice husks with a maximum at 1089 cm^{-1} decreases its intensity in the spectrum of the pyrolysed husks as a consequence of the destruction of the hydrocarbon component. In principle this band is typical of tridymite, but it is also connected with vibrations of the C-OH bond and it is characteristic of the C–O–C type of structure of the material.

The treatment of the 1S1 sample with HF acid leads to removal of SiO_2 from the composition of the material, but it does not eliminate the other inorganic compounds. Some weak bands are still observed in the spectrum of the sample 1S2 in the low wavelength region, accounting for the presence of Me–O bonds. Fig. 3a, 3b represents the XRD patterns of raw rice husks and those of the sample series 1S (3a) and 2S (3b).

The XRD data are typical of lignin-cellulose material (RH). The double diffraction maximum reveals the presence of cellulose, while the broadening of the peak is connected with the lignin component and with the hydrated amorphous silica, contained in the rice husks [33, 34].

In the XRD patterns of the precursors 1S2, 1S2, as well as in those of the activated materials two widely stretching peaks are observed – at about 24º and at 42.8º. The broad peak at 2θ value of 24º is representing the (002) graphite basal plane. The weaker broad peak at 43º indicates that the (100) and (101) peaks have merged to yield a single reflection demonstrating a relatively higher degree of randomness in the materials. In the pattern of 2S2 precursor the second peak is not so well defined as in the activated materials 2S3, 2S4 and 2S5. Most probably this peak correlates with the greater activated surface of the carbon materials. In the cases of the samples 2S2 and 2S3 the presence of elemental silicon is observed. This can be explained by the nature of the starting material as well as by the conditions of preparation of the sample 2S3.

The change in the value of the specific surface area, the sorption capacity with respect to iodine, the ash content and the pore volume in the process of treatment and activation of the rice husks are represented in Table 3.

Depending on the sequence of the treatment steps of the rice husks precursors are obtained having different specific surface area: 495 $m^2 \cdot g^{-1}$ (1S2), in the cases when the pyrolysis is carried out before the treatment with HF acid and 105 $m^2 \cdot g^{-1}$ (2S2), when the HF acid treatment precedes the pyrolysis. After elimination of the silica the specific surface area of the rice husks grows up to seven times higher value and after the pyrolysis – up to twenty times higher. The activation with carbamide, NaOH and $ZnCl_2$ results in an increase of the specific surface area up to thirteen times. The highest specific surface area was displayed by the samples, obtained by activation with carbamide and NaOH. The materials activated with carbamide, 2S3 and 1S3, have low ash content. This is due to the fact that the carbamide is decomposed without leaving any residual at the temperature of activation. Moreover, the carbamide is often used in its quality of pyrogenic agent in the case of preparation of substances with a definite morphology [36].

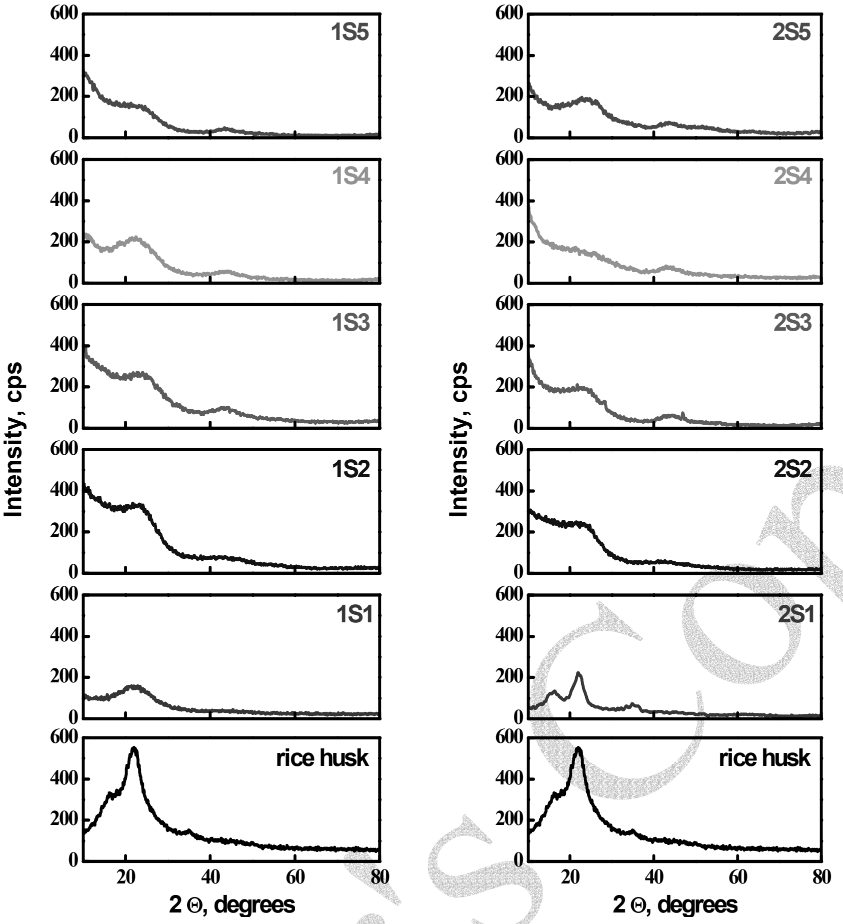

Fig. 3. XRD pattern of raw rice husk (RH) and of the samples 1S (a) and 2S (b).

Table 3. The pore volume, ash content, B.E.T. surface area and adsorption capacities of 2S and 1S series.

Sample code	Treatment conditions	Specific surface area, B.E.T., m^2·g^{-1}	Adsorption capacity, mgJ$_2$·g^{-1}	Ash content, %	Pore volume, cm^3·g^{-1}			
					Micro	Meso	Macro	Total
1S1	Pyrolysis	70	115	44	-	-	-	-
1S2	Desilicification	495	544	0.46	-	-	-	-
1S3	Activation with urea	1229	983	1.5	0.44	0.03	0.23	0.70
1S4	Activation with NaOH	1264	1028	18	0.62	0.08	0.04	0.74
1S5	Activation with ZnCl$_2$	1206	1085	2.0	0.34	0.27	0.12	0.73
2S1	Desilicification	5	-	0.34	-	-	-	-
2S2	Pyrolysis	105	120	0.84	-	-	-	-
2S3	Activation with urea	1259	1113	0.88	0.48	0.06	0.27	0.81
2S4	Activation with NaOH	1273	1018	20	0.60	0.11	0.08	0.79
2S5	Activation with ZnCl$_2$	888	844	4.8	0.24	0.31	0.13	0.68

It is known that the carbonization at higher temperature leads to formation of less stable and inactive carbon structure, which is connected with the presence of small quantities of oxygen-containing groups, due to which the materials have low porosity [26].

The probable mechanism of activation of the carbon material is associated with the interaction of carbamide with the OH and COOH groups, whereupon the –NHCONH$_2$ and the –CONHCONH$_2$ groups are being obtained. The latter groups at a temperature of 700ºC and in the absence of air decompose into NH$_3$ and CO$_2$. Thereupon part of the nitrogen of the carbamide can be included in the structure of the carbon, forming the so called diazo groups (–N=N–). A more detailed insight into the mechanism of activation of the pyrolysed carbon material with carbamide (with removal of the ash in advance) will be the subject of our future investigation.

The higher ash content of the samples, obtained using sodium hydroxide (S4), is connected with the specific mechanism of activation in this case. The carboxylic acids and methoxy phenols, obtained during the preliminary pyrolysis of the rice husks, interact with NaOH whereupon the respective sodium salts are being obtained. It is also possible that a reaction is occurring between the alkaline base and the silica that still remains in the material.

The decrease in the ash content of the samples, obtained using $ZnCl_2$ after their treatment with hydrochloric acid (S5), shows that in the process of activation the zinc chloride in its quality of Lewis acid probably plays the role of a catalyst.

The experimental results prove that the sequence of the treatment steps of the rice husks does not affect the value of the specific surface area of the samples, prepared by activation with carbamide and NaOH, while the area of the samples, obtained by activation with $ZnCl_2$ depends on the treatments steps sequence. This effect is probably due to differences in the mechanism of activation when using different substances [37].

The sorption capacity of the carbon materials with respect to iodine grows up with the increase of the BET specific surface area in a way, which is not proportional. The obtained results can be explained based on a decrease in the pore radius with the increase of the specific surface area. Taking into account the fact that the area, occupied by the adsorbed nitrogen molecule (16.2 $Å^2$), is smaller than the area, occupied by the iodine molecule (27.0 ± 10 $Å^2$) and that the diameters of the pores of the carbon materials for adsorption of the two molecules are greater than 0.4 and 0.6 nm respectively, then we can state that with the increase of the specific surface area the number of micropores with dia-meter below 0.6 nm is increased too.

The total pore volume of the obtained carbon materials varies from 0.68 up to 0.81 $cm^3 \cdot g^{-1}$ and it grows up with the increase of the specific surface area. The greater volume of the macropores of the materials, activated with carbamide, is connected with the more intensive gas evolution in the case of using this activating agent.

The obtained results have practical importance in view of selecting the appropriate activating agent for synthesis of carbonaceous materials with variety of morphology, which can find a different usage in the practice.

CONCLUSION

The results of the investigation carried out show the effect of preliminary removal of silica and the use of urea as activating agent on the specific surface area and on the ash content of porous carbon materials, obtained from rice husks. The sequence of the treatment steps of rice husks influences considerably the value of the specific surface area of the precursors. In the cases of applying carbamide and NaOH as activating agents, the treatment sequence does not affect the surface area of the final product. Some influence on the value of this parameter is observed only in the case of using $ZnCl_2$ as activating agent.

The samples of carbon material, activated with carbamide, possess the highest specific surface area – 1259 $m^2 \cdot g^{-1}$ and 1229 $m^2 \cdot g^{-1}$, the lowest ash content – below 2%, iodine adsorption capacity 1133 $mgJ_2 \cdot g^{-1}$ and 983 $mgJ_2 \cdot g^{-1}$ and total pore volume is 0.81$cm^3 \cdot g^{-1}$ and 0.70 $cm^3 \cdot g^{-1}$.

The carbon materials, activated with carbamide, have larger volume of macropores in comparison to the rest of the carbon materials, due to intensive evolution of gas during the decomposition of carbamide in the course of activation treatment.

In view of the high specific surface area and the low ash content, the carbon materials, prepared by us, can find a practical application in all fields in which active carbons are used. It is clear that a practical application is a subject of thorough investigations for every specific case of usage of these materials.

Acknowledgements: *The authors gratefully acknowledge the financial support by the Bulgarian Science Foundation (Contract TKH-1705/07) and the National Centre for Advanced Materials UNION.*

REFERENCES

1. D. F. Quinn, J. A. Macdonald, *Carbon*, **30**, 1097 (1992).
2. O. N. Kononova, A. G. Kholmogorov, A. N. Lukianov, *Carbon*, **39,** 383 (2001).
3. S. A. Dastgheib, D. A. Rockstraw, *Carbon,* **39**, 1849 (2001).
4. H. Shi, *Electrochim. Acta*, **41**,1633 (1996).
5. G. Salitra, A. Soffer, L. Eliad, Y. Cohen, *J. Electrochem. Soc.*, **147**, 2486 (2000).
6. C. T. Hsieh, H. Teng, *Carbon*, **40**, 667 (2002).
7. H. Teng, Y. Chang, C. T. Hsieh, *Carbon*, **39**, 1981 (2001).
8. J. Dias, M. Alvim-Ferraz, M. Almeida, J. Rivera-Utrilla, M. Sanchez-Polo, *J. Environ. Management*, **85**, 833 (2007).
9. O. Ioannidou, A. Zabaniotou, Renew. Sustain. Energ. Rev., **11**, 1966 (2007).
10. V. Minkova, G. Angelova, M. Goranova, L. Ljutzkanov, V. Litchev, Bulg. Chem. Commun., **23**, 85 (1990).
11. W. Xing, J. S. Xue, J. R. Dahn, *J. Electrochem. Soc.*, **143**, 3046 (1996).
12. A. Gibaud, J. S. Xue, J. R. Dahn, *Carbon,* **34**, 499 (1996).
13. W. Xing, R. A. Dunlap, J. R. Dahn, *J. Electrochem. Soc.*, **145**, 62 (1998).

14. E. Peled, V. Eshkenazi, Y. Rosenberg, *J. Power Sources*, **76**, 153 (1998).
15. S. Yamada, H. Imoto, K. Sekai, M. Nagamine, in: Proc. 191st Meeting of the Electrochemical Society, May 1997, Montreal, Canada, p. 85..
16. J. A. Amick, *J. Electrochem. Soc.*, **129**, 864 (1982).
17. N. K. Sharma, S. Williams, Z. Zangwil, *J. Amer. Ceram. Soc.*, **67**, 715 (1984).
18. UN Food and Agriculture Organization (FAO); http://faostat.fao.org .
19. Y. Guo, J. Qi, Y. Jiang, S. Yang, Z. Wang, H. Xu, *Mater. Chem. Phys.*, **80**, 704 (2003).
20. G. T.-K. Fey, Ch.-L. Chen, *J. Power Sources*, **97-98**, 47 (2001).
21. J. Laine, S. Yunes, *Carbon*, **30**, 601 (1992).
22. Z. Hu, M. Srinivasan, Y. Ni, *Carbon*, **39**, 877 (2001).
23. D. Lozano-Castello, M. A. Lillo-Rodenas, D. Cazorla-Amoros, A. Linares-Solano,*Carbon*, **39**, 741 (2001).
24. Y. Guo, K. Yu, Z. Wang, H. Xu, *Carbon*, **41**, 1645 (2000).
25. D. Kalderis, S. Bethanis, P. Paraskeva, E. Diamadopoulos, *Bioresour. Technol.*, **99**, 6809 (2008).
26. C. Yun, Y. Park, C. Park, *Carbon*, **39**, 559 (2001).
27. A. Wilson, J. Dahn, *J. Electrochem. Soc.*, **142**, 326 (1995).
28. J. Xue, K. Myrtle, J. Dahn, *J. Electrochem. Soc.*, **142**, 2927 (1995).
29. BDS ISO 1171.
30. ASTM D 3860-89a.
31. A. Vlasov, V. Florinskaya, A. Venediktov, K. Dutova, V Morozov, E. Smirnova, Infrared Spectra of Inorganic Glasses and Crystals, Khimiya, Leningrad, 1972, Ch. 1.
32. A. A. M. Daifullah, B. S. Girgis, H. M. H. Gad, *Mater. Lett.*, **57**, 1723 (2003).
33. W. Nakbanpote, B. Goodman, P. Thiravetyan, *Colloids Surf. A*, **304**, 7 (2007).
34. S. Hanna, L. Farag, N. Mansour, *Thermochim. Acta*, **81**, 77 (1984).
35. L. Kennedy, J. Vijaya, G. Sekaran, *Mater. Chem. Phys.*, **91**, 471 (2005).
36. W. Yang, G. Zhang, J. Xie, L. Yang, Q. Liu, *J. Power Sources*, **81-82**, 412 (1999).
37. O. Gyu, P. Chong, *Fuel*, **81**, 327 (2002).

ПОЛУЧАВАНЕ НА НИСКОПЕПЕЛЕН ПОРЕСТ ВЪГЛЕРОДЕН МАТЕРИАЛ ОТ ОРИЗОВИ ЛЮСПИ

С. А.Узунова[1]*, И. М. Узунов[2], С. В. Василев[3], А. К. Александрова[3], С. Г. Стайков[1], Д. Б. Ангелова[1]

[1] Химикотехнологичен и металургичен университет, бул. „Климент Охридски“ № 8, 1756 София
[2] Институт по обща и неорганична химия, Българска академия на науките,
ул. „Акад. Г. Бончев“, бл. 11, 1113 София
[3] Институт по електрохимия и енергийни системи, Българска академия на науките,
ул. „Акад. Г. Бончев“, бл. 10, 1113 София

Постъпила на 22 май 2009 г.;   Преработена на 18 декември 2009 г.

(Резюме)

Изследвано е влиянието на предварителното отстраняване на силициевия диоксид от изходната суровина и използването на нов активиращ агент (карбамид) върху свойствата на порест въглероден материал, получен чрез химично активиране на оризови люспи. Използвани са два различни подхода за получаване на порест въглероден материал с ниско пепелно съдържание, под 1% и специфична повърхност над 1000 m^2·g^{-1}. Първият се състои в пиролиз на оризови люспи при 450ºC с последващо отстраняване на силициевия диоксид с флуроводородна киселина и химическа активация при 700ºC (серия проби 1S). Вторият – в отстраняване на силициевия диоксид от суровите оризови люспи с последваща междинна пиролиза при 450ºC и химическа активация при 700ºC (серия проби 2S). Като активиращи агенти бяха използвани карбамид, NaOH и ZnCl$_2$.

Установено бе, че последователността на обработка на оризовите люспи влияе върху специфичната повърхност на двата прекурсора: 495 m^2·g^{-1} (за серия 1S) и 105 m^2·g^{-1} (за серия 2S) и специфичната повърхност на крайния продукт в зависимост от вида на използвания активиращ агент. Пробите от въглероден материал активирани с карбамид притежават съответно: специфична повърхност 1259 m^2·g^{-1} и 1229 m^2·g^{-1}; пепелно съдържание 0.88% и 1.5%; сорбционен капацитет на J$_2$ 1133 mgJ$_2$·g^{-1} и 983 mgJ$_2$·g^{-1}; общ обем на порите 0.81 cm^3·g^{-1} и 0.70 cm^3·g^{-1}.

Поради високата си специфична повърхност и ниско пепелно съдържание получените от нас въглеродни материали могат да се изследват като адсорбенти, носители на катализатори, активни материали за електрохимични източници на ток, включително и в суперкондензатори.