



Preparation of Rice Hull-Based Activated Carbon with Ammonium Nitrate

ISMAIL KILIC¹, YUKSEL BAYRAK^{2,*}, HARIKA TOPALLAR² and BUSE KARAGOZ²

¹Faculty of Education, Trakya University, Edirne, Turkey

²Department of Chemistry, Faculty of Science, Trakya University, Edirne, Turkey

*Corresponding author: Fax: +90 284 2358754; Tel: +90 284 2359592; E-mail: yukselbayrak@trakya.edu.tr

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The present study deals with the preparation of rice hull-based activated carbon with ammonium nitrate. The obtained carbon was activated at temperatures between 400 and 900 °C. The rice hull-activated carbon presented a BET surface area of 456.77 m² g⁻¹ and a pore volume of 0.2406 cm³ g⁻¹ at 600 °C. The adsorption and desorption average pore widths by BET method were found as 2.727 and 2.725 nm, respectively, whereas the Barret-Joyner-Halenda (BJH) adsorption and desorption average pore widths were 4.015 and 4.446 nm, respectively. Thus, it was found that rice hull-based activated carbon consisted of mesopores predominantly. These experimental results indicated the potential use of rice hull as a precursor in the activated carbon preparation process with ammonium nitrate. Moreover, the adsorption-desorption isotherm and the adsorption potential of the activated carbon that prepared at the optimum conditions were evaluated.

Key Words: Activated carbon, Ammonium nitrate, Rice hull, Pore volume, Pore width, Surface area.

INTRODUCTION

The world consumption of activated carbons is continuously increasing and new applications particularly those concerning environmental pollution remediation are being developed. Important applications of these are related to their use in water treatment for the removal of flavor, colour, odor and other undesirable organic impurities from water. Activated carbon is also used in industrial wastewater and gas treatment due to the necessity in environmental protection and also for material recovery purposes. Food and pharmaceutical industries are also a major consumer of activated carbon¹. Any cheap material with a high carbon content and low inorganics can be used as a raw material for the production of activated carbon. According to the literature survey, there have been many attempts to obtain low-cost activated carbon or adsorbent from agricultural wastes such as coconut shells², almond shells³, orange peel⁴, grape seeds³, apricot stones⁵, cherry stones³, olive stones⁶, peanut hull⁷, nut shells⁸, rice hulls⁹, oil palm shells¹⁰, sugarcane bagasse¹¹ and corn cob¹².

There are two basic processes to produce the activated carbon from carbonaceous materials *viz.*, physical and chemical. The precursor is developed into activated carbons using gases by carbonization in physical activation. Chemical activation can be accomplished in a single step by carrying out thermal decomposition of raw material with chemical reagents. This process is carried out with acidic reagents ZnCl₂¹³, H₃PO₄¹⁴,

HCl¹⁵ and H₂SO₄¹⁶ or with basic reagents KOH¹⁷, K₂CO₃¹⁸, NaOH¹⁹ and Na₂CO₃²⁰.

Rice hull is an agricultural waste material abundantly available in rice producing countries (especially in Trakya region of Turkey). They are the natural sheaths that form on rice grains during their growth. Since they are removed during the refining of rice, these hulls have no commercial interest.

The beneficiation of rice generates as by-product rice hull which corresponds to *ca.* 23 % of its initial weight. This hull can be used as a fertilizer in agriculture or as an additive for cement and concrete fabrication.

Due to its high silicon content, rice hull has become a source for preparation of elementary silicon and a number of silicon compounds, especially silica, silicon carbide. Raw rice hull has been employed to remove heavy metals from aqueous solution. The removal efficiencies were found to be both high and low for different adsorption conditions. This study also includes the adsorption of heavy metals by activated carbon made from rice hull²¹, activated rice hull²² and activated rice hull ash²³.

The objective of the present work is to prepare active carbon from rice hull by chemical activation with ammonium nitrate for a period of 0.5 h. After determination of optimum amount of ammonium nitrate and optimum temperature for the activation, the suitability and availability of this activation method have been studied by determining the specific surface area, the pore volume, the pore size, the adsorption-desorption

isotherm and the adsorption potential of the activated carbon that was prepared at the optimum conditions.

EXPERIMENTAL

Ammonium nitrate was purchased from Merck. Rice hull was supplied from a rice mill (Edirne, Turkey). It was washed thoroughly with distilled water to remove adhering soil and dust, dried at 110 °C overnight, cooled in a vacuum desiccator and then ground by a grinder.

Treatment of rice hull with ammonium nitrate and carbonization: Impregnation ratios had different amounts of NH₄NO₃ such as 5, 10, 15, 20, 25 and 30 g of NH₄NO₃ and fixed amount of rice hull as 5 g and they were well stirred in a 200 mL pyrex glass flask with 100 mL of distilled water using a magnetic stirrer for each experiment. Impregnation procedures were carried out at 70 °C under a reflux condenser for 1 h in 1100, 1200 and 1300 °C laboratory chamber furnace (CWF, Bristol, UK). It has maximum operating temperatures of 1100, 1200 and 1300 °C and a chamber capacity of 6 L and its temperature sensor is type K thermocouple. The mixture of impregnated rice hull with NH₄NO₃ as activating agent and water was filtered through a filter paper No. 40 (Whatman). Impregnated rice hulls on the filter paper were put into a ceramic vessel resistant to 1500 °C and then placed inside the muffle furnace when the muffle furnace temperature is heated to desired temperature. Hull samples were carbonized at different heats; 400, 500, 600, 700, 800 and 900 °C for 0.5 h. When the carbonization time was completed, the ceramic vessel was removed from the furnace and cooled in a desiccator. Activated carbons were sieved to obtain the desired particle size (1.00-1.25 mm).

A Tri Star 3020 (Micromeritics, Norcross, USA) surface analyzer was used to measure nitrogen adsorption-desorption isotherm at 77 K in the range of relative pressure (P/P⁰) 10⁻⁶ to 1. Before measuring, all samples were degassed at 300 °C for half an hour. The specific surface area was determined by the adsorption method of Brunauer-Emmett-Teller (BET). Adsorption and desorption cumulative pore volumes and pore sizes (as width) were measured by cumulative adsorption and desorption method of Barret-Joyner-Halenda (BJH).

High yields are desirable in activated carbon production and help to reduce production costs. The activated carbon yield obtained from rice hulls by chemical activation with NH₄NO₃ can be determined in the following equation²⁴:

$$\text{Carbon yield (\%)} = \frac{\text{Activated carbon weight}}{\text{Raw material weight}}$$

RESULTS AND DISCUSSION

Proximate analysis and chemical composition of rice hull and activated carbon: The fixed carbon content of raw rice hulls is higher than others and on the other hand carbon content is not very low. It is almost close to others as can be seen in Table-1. Proximate analysis and chemical composition of rice hull-based activated carbon and other biomasses are shown in Table-2.

Effect of the temperature on the carbonization: Table-3 shows the BET surface areas of activated carbons prepared from rice hull at various temperatures with different amounts of NH₄NO₃. These results demonstrate how activation temperature increases surface area until an optimum surface area value is obtained.

TABLE-1
PROXIMATE ANALYSIS AND CHEMICAL COMPOSITION OF RICE HULL AND OTHER RAW MATERIALS

	Almond shell ²⁵	Apple pulp ²⁶	Apricot stone ²⁵	Coconut shell ²⁷	Corn Cob ²⁸	Rice hull	Soybean oil cake ²⁹	Sunflower oil cake ³⁰
Proximate analysis								
Moisture content (%)	8.7	5.7	6.4	6.1	3.3	6.67	9.9	9.8
Volatile matter (%)	79.7	79.0	80.6	77.2	79.4	62.3	69.8	67.4
Fixed carbon (%)	–	–	–	22.1	9.0	22.5	14.4	17.6
Ash (%)	2.3	2.6	0.2	0.7	8.3	11.5	5.8	5.2
Chemical composition (wt %)								
C	54.7	49.6	51.5	50.2	45.5	40.9	44.5	46.6
H	7.5	8.4	6.3	5.7	6.1	5.2	6.3	6.1
N	0.3	1.0	0.2	1.12	0.6	0.4	8.2	4.5
O	37.4	38.2	41.9	42.6	47.8	36.8	40.5	42.4

TABLE-2
PROXIMATE ANALYSIS AND CHEMICAL COMPOSITION OF RICE HULL-BASED ACTIVATED CARBON AND OTHER BIOMASSES

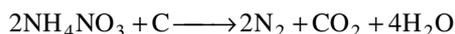
	Almond shell ²⁵	Apple pulp ²⁶	Apricot stone ²⁵	Coconut shell ³¹	Corn cob ²⁸	Rice hull	Soybean oil cake ²⁹	Sunflower oil cake ³⁰
Proximate analysis								
Moisture content (%)	1.8	–	1.6	–	–	3.2	–	–
Volatile matter (%)	4.9	–	3.7	–	–	11.8	12.3	17.5
Ash (%)	2.8	–	2.0	–	–	5.3	8.7	13.4
Fixed carbon (%)	–	–	–	–	–	62.8	79.1	69.0
Chemical composition (wt %)								
C	87.9	74.7	89.5	48.1	66.5	67.6	64.6	58.8
H	2.5	3.6	2.4	6.0	–	0.6	1.7	1.7
N	1.1	1.2	0.9	0.0	2.6	0.5	8.5	5.7
O	7.8	12.7	6.4	45.9	27.0	15.4	25.1	27.7

TABLE-3
BET SURFACE AREA OF RICE HULL-BASED ACTIVATED CARBON AT VARIOUS TEMPERATURES

t (°C)	5 g	10 g	15 g	20 g	25 g	30 g
	S/m ² g ⁻¹					
400	299.69	350.06	395.32	415.02	382.56	369.31
500	317.11	390.02	415.02	433.89	405.38	398.36
600	330.02	407.77	433.88	456.77	427.47	416.53
700	299.69	357.04	389.24	401.92	380.02	370.48
800	190.53	235.36	280.52	294.67	269.10	254.62
900	83.03	127.80	177.73	192.88	162.59	146.65

Since more burning occurs, amount of activated carbon decreases and high ash content generally arises after this value and the surface area values decrease at higher activation temperatures. Optimum amount of NH₄NO₃ and optimum temperature for activated carbon obtained from 5 g of rice hull were determined as 20 g of NH₄NO₃ and 600 °C, respectively. The highest BET surface area under these conditions was found as 456.77 m²/g. This value is higher than the value of 319 m²/g determined by Teker *et al.*³². They have prepared activated carbon from rice hulls by means of ZnCl₂.

Chemical activation mechanism during the carbonization: Thermal decomposition of ammonium nitrate under the action of carbon is as follows³³:



This reaction results in the formation of porous structure of activated carbon. Already, it was determined that the mesopores (2 nm < d < 50 nm) occurred on the surfaces of activated carbon obtained by carbonization of rice hulls at 600 °C.

Carbon yield and surface areas pore volumes and pore sizes: The activated carbon yield is in the range of 9.5-25.4 %, given in Table-4. The yield was observed to increase slightly from 400-600 °C, but to decrease from 600-900 °C. Since more

carbon burns off after 600 °C during activation, the activated carbon amount decreases. The adsorptive capacity of an activated carbon is related to its surface area, pore volume and pore size.

Table-4 demonstrate how activation temperature increases surface area until an optimum surface area value is obtained. Since more burning occurs, amount of activated carbon decreases and high ash content generally arises after this value and the surface area values decrease at higher activation temperatures as can be seen in Fig. 1.

The BET surface area of activated carbon is 456.77 m² g⁻¹ at 600 °C, whereas BJH adsorption and desorption surface area of pores are 170.71 and 189.79 m² g⁻¹, respectively. The data in Table-4 shows that the effects of activation temperature plays an important role on the surface areas of the resulting activated carbons.

The activation temperature affects not only the single point, BET, Langmuir, BJH adsorption and desorption cumulative surface areas (Fig. 1) but also pore volume (Fig. 2) and pore width (Fig. 3). The average pore volume increases at the activation temperature range of 400-600 °C but a decrease of average pore volume was observed after 600 °C (Fig. 2).

Fig. 3 shows the average pore width of activated carbons as a function of activation temperatures. The average pore

TABLE-4
CARBON YIELD, SURFACE AREA, PORE VOLUME AND PORE SIZE OF RICE HULL-BASED ACTIVATED CARBON AT DIFFERENT TEMPERATURES

Characteristics	400 °C	500 °C	600 °C	700 °C	800 °C	900 °C
Carbon yield (%)	19.2	21.7	25.4	18.6	13.3	9.5
Surface areas						
Single point surface area (m ² /g)	421.35	444.80	466.42	405.02	301.29	198.17
BET surface area (m ² /g)	415.02	433.88	456.77	401.93	294.68	192.88
Langmuir surface area (m ² /g)	551.47	574.61	606.86	536.34	390.21	255.58
BJH adsorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm width (m ² /g)	84.14	130.57	170.71	112.48	70.46	26.13
BJH desorption cumulative surface area of pores between 1.7000 nm ve 300.0000 nm width (m ² /g)	102.75	150.96	189.79	127.77	83.96	34.28
Pore volumes						
Single point adsorption total pore volume of pores less than 120.0000 nm width (cm ³ /g)	0.0994	0.1816	0.2406	0.2629	0.2667	0.2740
Single point desorption total pore volume of pores less than 65.0000 nm width (cm ³ /g)	0.0993	0.1816	0.2405	0.2628	0.2664	0.2739
BJH adsorption cumulative volume of pores between 1.7000 nm and 300.0000 nm width (cm ³ /g)	0.0158	0.0687	0.1067	0.1223	0.1391	0.1712
BJH desorption cumulative volume of pores between 1.7000 nm ve 300.0000 nm width (cm ³ /g)	0.0217	0.0740	0.1114	0.1286	0.1469	0.1791
Pore sizes						
Adsorption average pore width (nm) (4V/A by BET)	2.410	2.571	2.727	2.302	2.108	2.000
Desorption average pore width (nm) (4V/A by BET)	2.409	2.567	2.725	2.301	2.107	2.000
BJH adsorption average pore width (nm) (4V/A)	3.674	3.804	4.015	3.558	3.145	2.900
BJH desorption average pore width (nm) (4V/A)	4.073	4.230	4.446	3.985	3.595	3.300

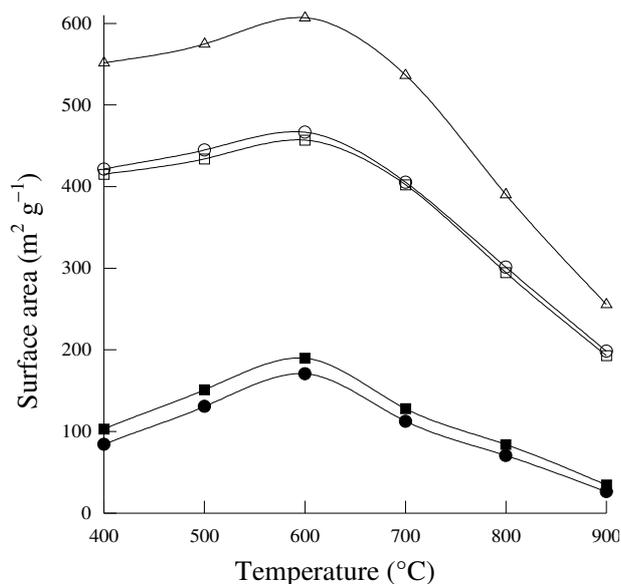


Fig. 1. Influence of activation temperature on the single point surface area (○), BET surface area (◻), on the Langmuir surface area (Δ), on the BJH adsorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm widths (●), on the BJH desorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm widths (■)

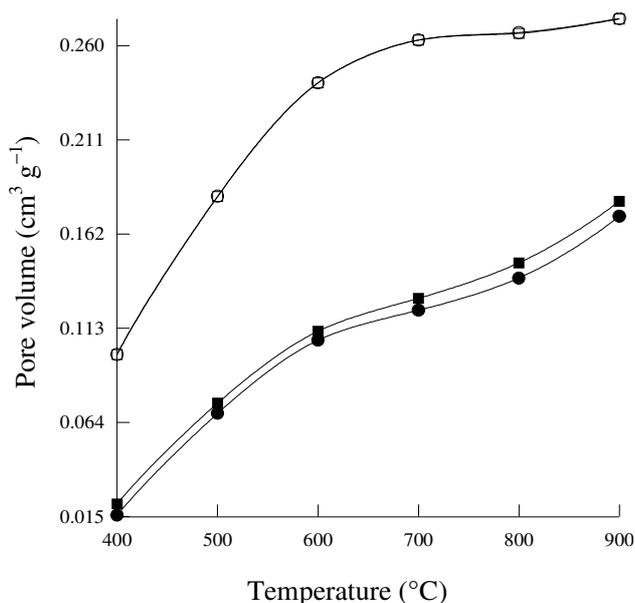


Fig. 2. Influence of activation temperature on the single point adsorption total pore volume of pores less than 120.0000 nm width (○), on the single point desorption total pore volume of pores less than 65.0000 nm width (◻), on the BJH adsorption cumulative volume of pores between 1.7000 nm and 300.0000 nm widths (●), on the BJH desorption cumulative volume of pores between 1.7000 nm and 300.0000 nm widths (■)

width decreases with raising the activation temperature up to 600 °C and then increases with further rise in the temperature.

The BJH method is the most popular method used for the evaluation of the mesopore size distribution. The pore sizes are classified in accordance with classification adopted by the International Union of Pure Applied Chemistry (IUPAC, 1982), that is, micropores (pore width or pore diameter ($d < 2$ nm), mesopores ($2 \text{ nm} < d < 50$ nm) and macropores ($d > 50$ nm).

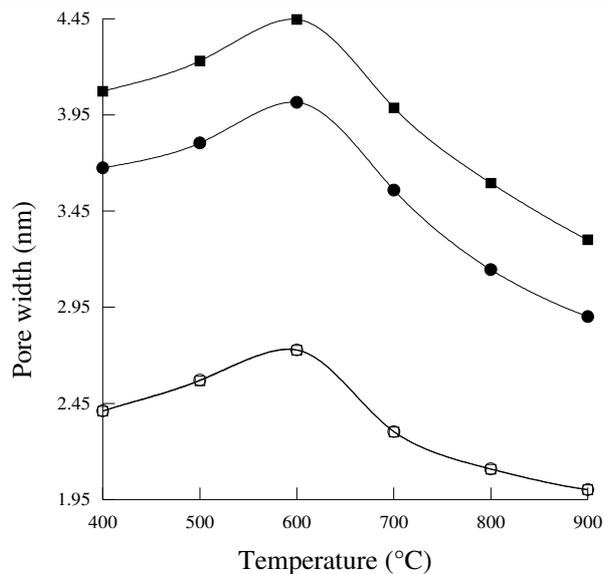


Fig. 3. Influence of activation temperature on the adsorption average pore width (4V/A by BET) (○), on the desorption average pore width (4V/A by BET) (◻), on the BJH adsorption average pore width (4V/A) (●), on the BJH desorption average pore width (4V/A) (■)

The micropores can be divided into ultra-micropores ($d < 0.7$ nm) and super-micropores ($0.7 \text{ nm} < d < 2$ nm). Because of the larger sizes of liquid molecules, the adsorbents for liquid phase adsorbates should have predominantly mesopores in the structure³⁴.

Rice hull-based activated carbon has a wide pore size distribution giving wide distribution of surface area. The data in Table-4 show that the single point adsorption total pore volume of pores less than 120.0000 nm width and desorption total pore volume of pores less than 65.0000 nm width are 0.2406 and 0.2405 cm³ g⁻¹, respectively, whereas the BJH adsorption cumulative volume of pores between 1.7000 and 300.0000 nm width and the BJH desorption cumulative volume of pores between 1.7000 nm ve 300.0000 nm width are 0.1067 and 0.1114 cm³ g⁻¹, respectively, at 600 °C.

The analysis of the BJH adsorption pore distribution shows that the micropores ($d < 2$ nm) have a total pore area of about 20 %, mesopores account for about 78 % and that the macropores are *ca.* 2 %. The desorption pore distribution shows that the mesopores account for 99 % of the pore area³⁵.

The adsorption and desorption average pore widths by BET method are found to be 2.727 and 2.725 nm, respectively, at 600 °C, whereas the BJH adsorption and desorption average pore widths are 4.015 and 4.446 nm, respectively. Thus, it is found that activated carbon from rice hull consists of mesopores predominantly. This is what is desirable for the liquid phase adsorptive removal of metal ions. The 99 % pore area attributed to mesopores during desorption indicates the predominance of mesopores in adsorption process.

N₂ adsorption-desorption isotherms of activated carbon: Identifying pore structure of adsorbents by the adsorption of inert gases such as nitrogen is essential before liquid sorption experiments³⁶. Fig. 4 illustrates adsorption (mesopores ($2 \text{ nm} < d < 50$ nm)) for the adsorption and desorption average pore widths to be 2.727 and 2.725 nm, respectively, by the BET method at 600 °C.

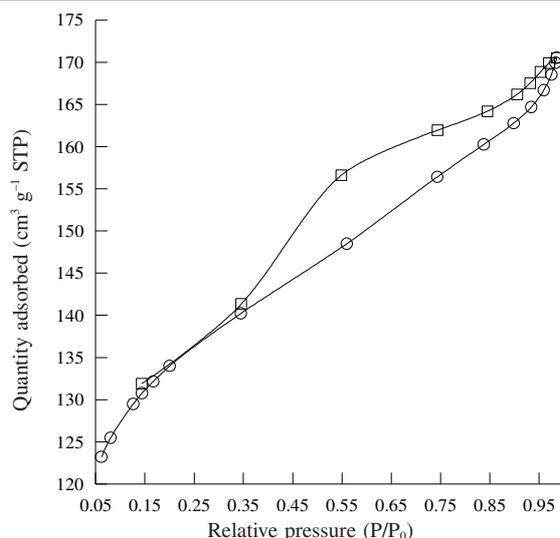


Fig. 4. Influence of relative pressure (P/P_0) on the adsorption average pore width (4V/A by BET) (○), on the desorption average pore width (4V/A by BET) (□)

Adsorption potential energy of activated carbon: The Polanyi adsorption potential energy theory for gases may be summarized as follows: within the range of the attractive forces of the solid surface (the adsorption space) the potential energy of a given gas is reduced, in relation to its value at infinity, by an amount ϵ (the adsorption potential) that is for a given gas depends on proximity to the solid surface³⁷. The filling of pores by adsorption in micropore range may be described by the potential theory. According to Polanyi³⁸ the adsorption potential expresses the work of temperature independent from dispersion forces. The change in free energy, when one mole adsorbate is transferred from vapor state to the adsorbed state, is

$$\Delta G = -\epsilon = RT \ln \frac{P}{P^0}$$

where P/P^0 is relative pressure, P is the (equilibrium) pressure of the gas and P^0 is the saturation pressure (P^0)³⁷. A plot of the volume of the filled adsorption space, V , against the adsorption potential, ϵ , gives the characteristic curve which is independent of temperature (Fig. 5).

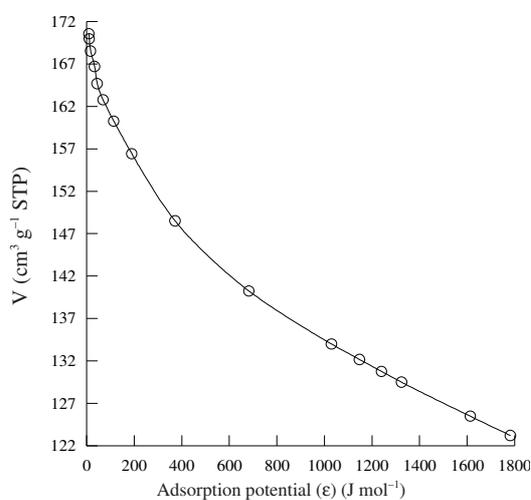


Fig. 5. Quantity adsorbed as volume (in $\text{cm}^3 \text{g}^{-1} \text{STP}$) versus adsorption potential ($\epsilon/\text{J mol}^{-1}$) for nitrogen on the activated carbon prepared from rice hull with ammonium nitrate

The values of the adsorption potentials are almost between 0.009 and 1.8 kJ mol^{-1} . These values are lower than those in the study by Canel *et al.*³⁹, because the pores in the present study are dominantly mesopores.

Conclusion

It has been seen that rice hull-based activated carbon prepared with ammonium nitrate has $456.77 \text{ m}^2 \text{g}^{-1}$ by the BET method at 600°C . The adsorption and desorption average pore widths by the BET method were found to be 2.727 and 2.725 nm, respectively. It was found that activated carbon consisted of mesopores predominantly because these values are between 2 and 50 nm. Thus, it is suitable for the liquid phase adsorptive removal of metal ions. On the other hand, the values of the adsorption potential energy are not very high, because the filling of pores by adsorption is related to the micropores, that is, rice hull-based activated carbon has more mesopores than micropores.

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