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Synthesis and characterization of activated carbons obtained from nutshells

Diana Mańko^{a,c}, Mariusz Barczak^b and Anna Zdziennicka^a

Faculty of Chemistry, ^aDepartment of Interfacial Phenomena,

^bDepartment of Theoretical Chemistry

Maria Curie-Skłodowska University

M. Curie-Skłodowskiej Sq. 3, 20-031 Lublin, Poland

^cmanko_diana@interia.pl

Walnut and hazelnut shells were used to prepare activated carbons using potassium hydroxide as an activation agent. The obtained activated carbons presented a specific surface areas of 1661 and 1322 m²/g and pore total volumes of 0.80 and 0.65 cm³/g, respectively. Moreover, the obtained activated carbons presented high quantity of micropores in their structure and that is why they have a great potential for environmental applications and they could be an alternative to commercially available activated carbons from the viewpoint of adsorption capacity. This paper proves that walnut and hazelnut shells have got a large potential as precursors to obtaining activated carbons and they could be successfully converted into a well-developed porous materials by chemical activation.

1. INTRODUCTION

Activated carbons are popular porous adsorbents with high surface area (more than 500 m²/g) and turbostratic structure [1]. Crystal structure and the most important properties of activated carbons depend on the type of organic precursor used to produce them and the conditions prevailing during the whole process of preparation of activated carbons. Almost any

carbonaceous source material may be used as a raw material for the preparation of activated carbons. The most commonly used raw materials for the production of commercial activated carbons are wood, charcoal, soft coal, petroleum coke, lignite and peat [2]. The demand for activated carbon is growing and production and regeneration of activated carbons produced from mentioned before raw materials are expensive. Therefore, such agriculture by-products as nutshells, fruit stones, corncobs or spirit lees are more frequently used as precursors of activated carbons. These materials are usually high in carbon content and low in inorganic matter content [3, 4]. A large number of activated carbons produced from waste materials can replace commercial activated carbons due to their low-cost, well-developed structure, high surface area and high efficiency in adsorption of both gases and solutes from aqueous solutions. Moreover, the production of activated carbons from agriculture waste materials (which are generated in large quantities) allows to dispose them and convert into valuable adsorbents with a reasonable cost [5, 6].

Activated carbons can be obtained by physical or chemical activation of raw material. The physical activation process consists of two stages. The first one is the pyrolysis of raw material in high temperature (500-800°C) without contact with oxygen or other chemical reagent. Thus, this process is called carbonization. After the carbonization, in the second stage, the prepared char is reacting with water steam, carbon dioxide or air, usually at a high temperature (800-1000°C) [7, 8].

In one-step chemical activation the raw material is treated (mixed or impregnated) with a chemical reagent, and then this mixture is pyrolyzed in an inert atmosphere (the activation and the carbonization processes are carried out at the same time) at a lower temperature and a shorter time than those used in the physical activation process [9]. During the chemical activation, the raw material reacts with the chemical agent, which can be: salt (ZnCl_2 , K_2CO_3), acid (HNO_3 , H_2SO_4 , H_3PO_4) or hydroxide (NaOH , KOH) [10]. The chemical activation needs a washing step at the end of the whole process because the porosity created in the carbon structure is blocked by the chemical compounds, which have to be removed from the resultant activated carbon to acquire required porosity.

As a result of the activation process, a much richer carbon content material with more ordered and more developed structure than the precursor is obtained [11]. The nature of the precursor, carbonization process conditions (heating rate, time and final temperature of pyrolysis) and activation process conditions (type of activation agent, the chemical

reagent to raw material ratio, heat treatment and washing-step at the end of the process) have an effect on the chemical and properties and the porous structure of the produced activated carbons.

In this paper, a method for preparing activated carbons from the walnut and hazelnut shells by chemical activation using potassium hydroxide as an activation agent has been described. The chemical activation is an effective method to obtain activated carbons with a higher surface area and narrower pore distribution than those prepared in a physical one [12]. Moreover, KOH is a strong base which diffuses into carbon layers, destroys a textural structure of raw material and creates microporosity in the carbon structure (microporosity is a result of a series of chemical reactions and intercalation of alkali metal in the material structure), and it is found to be the most effective alkali hydroxide in the preparation of activated carbons with a well-developed structure [6, 11, 13]. The chemical activation by alkalis involves the hydroxide reduction and carbon oxidation to generate porosity. In such case, KOH is an activation agent which promotes oxidation reactions and catalyzes them [12, 13]. The reactions during KOH activation can take place in the following way [14]:



and then some surface oxygen complexes can be generated, which are responsible for the continuation of carbon gasification and release of the gaseous substances [11].

The aim of this paper is to investigate the influence of the type of raw material and the selected conditions that prevail during the process of preparation of activated carbons on the pore structure and surface chemistry of obtained adsorbents. The obtained from adsorption isotherms results were also compared with the values of the same textural parameters calculated for the commercially available activated carbon – Norit SX-2.

2. MATERIALS AND METHODS

2. 1. *Preparing activated carbons*

Two kinds of nutshells were used as precursors to prepare activated carbons: the walnut and hazelnut shells.

Before the carbonization, the nutshells were crushed and weighed. Next, the particulate material was placed in a quartz boat in the heating part of the furnace type PRC 20M and heated up to the carbonization temperature (500°C) under a nitrogen gas flow at 300 cm³/min with a heating rate of 10°C/min. This temperature was maintained for 2 hours. After this time, the resulting char was cooled down to room temperature, weighed and ground to fine powder in a mortar. The resulting powder was mixed with solid potassium hydroxide (weight ratio of 1:2) and left for 30 minutes at room temperature. After this time, the resulting sample was again placed in the furnace and pyrolyzed under the same nitrogen gas flow and heating rate. The temperature during the process was changed at first from room temperature to 300°C with a residence time of 2 hours and next from 300 to 800°C with the same residence time. After the pyrolysis, the resulting sample was cooled down to room temperature under the nitrogen gas flow, and then it was washed to remove the residual KOH with 0.1 mol/dm³ hydrochloric acid. After 1 hour, the excess of the acid was leached out by washing with distilled water until the pH of the filtrating solution was neutral (the wash waters were tested with solid AgNO₃ for the detection of chloride ions) and finally the cleaned material was dried in an oven for 12 hours at 110°C.

The activated carbons prepared from the walnut and hazelnut shells are designated WS and HS, respectively.

2.2. Characterization of the pore structure

The characteristic of the pore structure of the obtained activated carbons was determined from the nitrogen adsorption/desorption isotherms measured at -196°C on an automatic adsorption apparatus Micrometrics ASAP 2405N. The obtained isotherms were used to calculate the specific surface areas ($S_{Langmuir}$ and S_{BET}) using the Langmuir equation and the BET (Brunauer-Emmet-Teller) one. The t -plot and BJH methods were applied to calculate the total pore volumes (V_{Total}), the micropore volumes (V_{micro}) and the pore size distributions. At the end, the average pore diameters ($d_{Average}$) were determined.

The textural parameters of the commercial activated carbon (Norit SX-2) were calculated by the same way for a comparison between the textural properties of widely used commercial carbon and the obtained activated carbons.

2.3. Chemical characterization

The surface chemistry of the obtained activated carbons was studied by means of Fourier transform infrared (FT-IR) spectroscopy. FT-IR spectra were recorded on a 1725X Perkin-Elmer spectrophotometer at room temperature with a resolution of 4 cm^{-1} and KBr discs.

3. RESULTS AND DISCUSSION

Two series of activated carbons were prepared by the chemical activation of walnuts and hazelnuts shells with potassium hydroxide as an activation agent.

Figure 1 shows the nitrogen adsorption/desorption isotherms for the WS, HS and Norit SX-2 activated carbons. The shapes of both obtained for HS and WS adsorption isotherms are Type I in the IUPAC classification. This means that at low values of relative pressure a rapid linear increase in nitrogen adsorption followed by a plateau can be observed. Type I of the isotherm is called the Langmuir isotherm and it indicates that the tested material is mainly microporous [15].

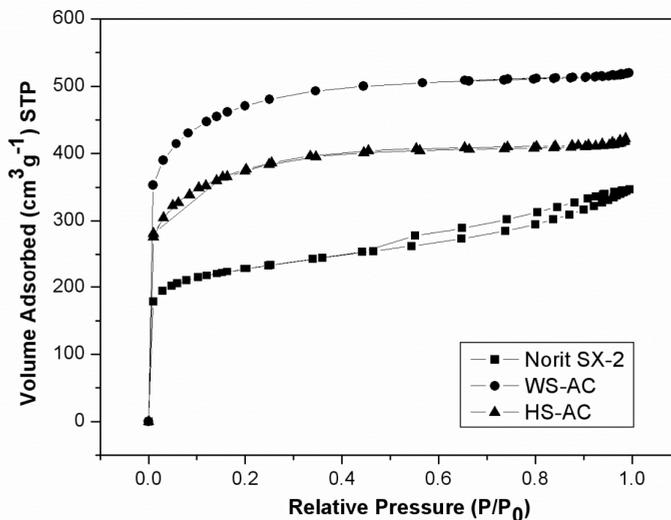


Fig. 1. N_2 adsorption/desorption isotherms at 77 K of the WS, HS and Norit SX-2 activated carbons.

The adsorption isotherm for Norit SX-2 is structurally different from those obtained for the WS and HS activated carbons – it rapidly increases at low values of relative pressure but for higher values of relative pressure

it shows no plateau but further gradual increase until it reaches $p/p_0=1$ [13]. Such an increase in the whole range of the relative pressure suggests that Norit SX-2 is a mainly microporous material with a certain mesoporosity development, and the presence of the hysteresis loop (type H4), which occurs at around 0.45 relative pressure, confirms the high content of mesopores in the structure of the adsorbent. The obtained results for the WS and HS activated carbons, for which the major adsorption occurs only below a very low pressure ($p/p_0 = 0.1$), indicates that their pore size distributions are uniform in contrast to the commercial Norit SX-2, for which the pore size distribution is heterogeneous [8, 16].

The obtained from adsorption/desorption isotherms results were also used to calculate the specific surface area of WS, HS and Norit SX-2 activated carbons by means of the BET and the Langmuir equations. The BET equation is commonly used to calculate the specific surface area of porous adsorbents and it can be applied in the range of the relative pressure in which the plot of $1/[V(p_0/p - 1)]$ vs. p/p_0 is linear. It is better to use the Langmuir equation to calculate the specific surface area of microporous adsorbents (for which it is often difficult to establish the relative pressure range in which the BET equation may be applied). The Langmuir method is based on the theory of monomolecular adsorption and this type of adsorption is characteristic of the microporous adsorbents [17, 18].

The values of the specific surface areas calculated from BET and Langmuir isotherms are summarized in Table 1. The values of $S_{Langmuir}$ for all the examined carbons are higher than the values of S_{BET} . The highest values of the specific surface areas are observed for WS activated carbon and at the same time the values of $S_{Langmuir}$ and S_{BET} for both obtained activated carbons are much higher than those for the commercial Norit SX-2.

The values of the total pore and micropore volumes and the average of the pore diameters of examined carbons are also summarized in Table 1.

Table 1. Textural parameters of the WS, HS and Norit SX-2 activated carbons.

Sample code	S_{BET} ($m^2 g^{-1}$)	$S_{Langmuir}$ ($m^2 g^{-1}$)	V_{Total} ($cm^3 g^{-1}$)	V_{micro} ($cm^3 g^{-1}$)	$d_{Average}$ (\AA)
WS	1661	2098	0.80	0.40	24
HS	1322	1671	0.65	0.28	32
Norit SX-2	804	1011	0.53	0.21	41

The experimental results indicate that the total pore and micropore volumes of WS activated carbon are higher than those of HS one. The inverse relationship is observed for an average pore diameter which is lower for WS than for HS activated carbon. The textural parameters of the obtained activated carbons may be compared to those represented by the commercial activated carbon. Norit SX-2 has got a smaller surface areas, smaller total pore and micropore volumes and higher average pore diameter compared to the obtained activated carbons. The highest ratio of the micropore volume to the total pore volume (0.5) is observed for WS activated carbon. This ratio for HS (0.43) and Norit SX-2 (0.4) is much lower, but still the share of micropores in their structure is significant.

Finally, the pore distribution was also calculated from the nitrogen adsorption data. The porosity and the pore size distribution in the activated carbons depend on the type of raw material and the activation process conditions (including the type of an activation agent). The pore size distributions of both obtained activated carbons are given in Fig. 2 and they characterize the structural heterogeneity of the obtained materials.

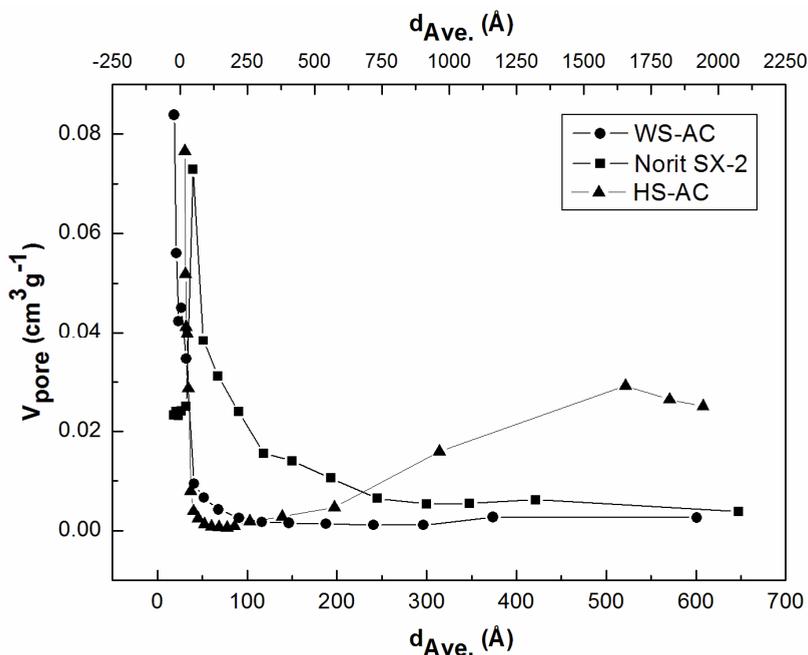


Fig. 2. Pore size distribution of the WS, HS and Norit SX-2 activated carbons.

The walnut shells are more susceptible to develop microporosity on activation with potassium hydroxide than hazelnut shells. For the

commercial Norit SX-2, a wider and more heterogeneous pore size distribution (also shown in Figure 2) is observed. In the structure of the resultant carbons and commercial activated carbon there are micropores ($<20\text{\AA}$) located between carbon layers, mesopores ($20\text{-}500\text{\AA}$) and macropores ($>500\text{\AA}$) in different proportions [19]. The pore size distributions indicate that in the structure of the WS activated carbon there are pores with the sizes ranging from 18 to 600\AA and most of them are micropores with the sizes smaller than 20\AA and small mesopores with the sizes $20\text{-}40\text{\AA}$ (10% of all the pores are pores with the sizes of $18\text{-}20\text{\AA}$). In the structure of the HS activated carbon there are pores with the sizes ranging from 18 to 1950\AA , and as in the case of WS activated carbon, there are a lot of micropores and small mesopores (12% of all the pores are pores with the sizes of $18\text{-}20\text{\AA}$), but in contrast to the WS activated carbon HS has got a lot of pores with the sizes more than 500\AA (macropores). At the same time in the structure of Norit SX-2 there are pores with the sizes ranging from 18 to 650\AA and most of them are mesopores with the sizes of $35\text{-}50\text{\AA}$ (12% for all the pores). It can be seen from the graph presenting the pore size distribution of Norit SX-2 that the porosity of this carbon is very heterogeneous and in its structure there are a lot of pores with different sizes (the pore distributions of the WS and HS activated carbons are narrower).

Essentially microporous WS and HS activated carbons probably have a better adsorption capacity than Norit SX-2 because the adsorption capacity of porous adsorbents largely depends on the amount of micropores that are present in their structure [13].

The chemical characterization of the obtained activated carbons was studied by FT-IR spectroscopy in order to identify what kind of surface functional groups are at their surfaces. Figure 3 shows the FT-IR spectra for the obtained activated carbons.

Both samples show the broadband adsorption spectra around $3700\text{-}3000\text{ cm}^{-1}$ typical for O–H stretching vibrations in hydroxyl groups associated with the surface, or for O–H–O stretching vibrations in water molecules which could be adsorbed on the surface. Higher intensity of this band for the WS than HS activated carbon indicates its more hydrophilic character. Moreover, all the samples exhibit two weak peaks around 2850 and 2900 cm^{-1} which can be attributed to C–H stretching vibrations in the methyl group [20].

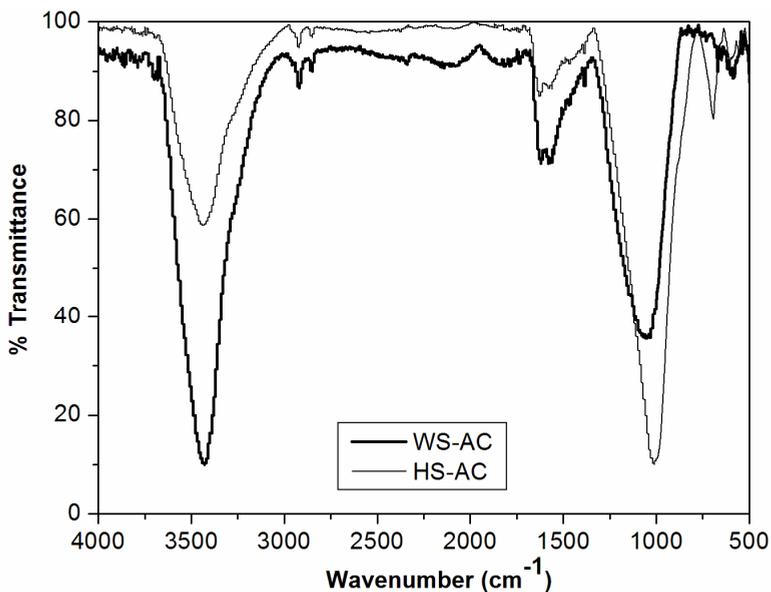


Fig. 3. FT-IR spectra of the WS and HS activated carbons.

The peaks around $1700\text{--}1350\text{ cm}^{-1}$, visible for both activated carbons, are probably the result of a combination of several bands characteristic for different types of vibrations: C=O stretching vibrations in the carbonyl or lactonic groups ($1650\text{--}1700\text{ cm}^{-1}$) [14], C=C aromatic ring stretching vibrations ($\sim 1600\text{ cm}^{-1}$), $-(\text{C}=\text{C})_n-$ bonds stretching vibrations in polyenes (1590 cm^{-1}), C-H stretching alkane ($1350\text{--}1400\text{ cm}^{-1}$), and also vibrations typical for the carboxyl-carbonate structures near the wavenumber of 1400 cm^{-1} [20, 21].

Strong and broad band for both activated carbons is observed around $1350\text{--}800\text{ cm}^{-1}$, and it can be attributed to C-O stretching vibrations in phenolic, carboxylic or ether groups which are dominant in the HS activated carbons (higher intensity of the band).

Moreover, for the HS activated carbon, the weak peak around 700 cm^{-1} is observed. It probably correspond with $-\text{COH}$ deformation vibrations or it could be related to the cyclic aromatic structures [20].

Probably at the surface of the resultant carbons there are oxygen groups like carbonyl, ether, alcohol, carboxyl and phenolic groups [22].

4. CONCLUSIONS

Highly microporous activated carbons with the presence of oxygenated functional groups at their surfaces were prepared from the walnut and hazelnut shells by the chemical activation with solid potassium hydroxide. The resultant activated carbons attained high values of the specific surface areas and micropore volumes up to 2.5 cm³/g. The obtained results indicated that the walnut and hazelnut shells could be great raw materials for the preparation of activated carbons with the large surface area and well-developed porosity.

It was also found that the obtained activated carbons had higher surface areas, narrower pore size distributions and more developed structures than commercial Norit SX-2. Therefore, they have also better adsorption properties and could be used in numerous fields which require the higher surface areas carbons, e.g. for gas storages or as an electrode materials for electric double layer capacitors and supercapacitors [7, 23].

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CURRICULA VITAE



Diana Mańko. Born in Radzyń Podlaski (Poland) in 1988. Graduated from Maria Curie-Skłodowska University in Lublin (2012, Department of Theoretical Chemistry). Since 2012 she has been a Ph.D. student in the Department of Interfacial Phenomena at UMCS. Currently she is carrying out research on physicochemical properties of water solutions of sugar-based surfactants, biosurfactants and their mixtures with different additives.



Mariusz Barczak. Born in Swidnik in Poland in 1978. Received his Ph.D. degree in 2007. Since 2007 he has been held a position of adjunct in the Department of Theoretical Chemistry of UMCS. He is a co-author of over 40 papers. Main fields of his interest are: synthesis, functionalization and investigation of porous silica, carbon and hybrid nanomaterials and their application as sorbents of heavy metal ions, phenols and biomolecules.



Anna Zdziennicka. Graduated from Maria Curie-Skłodowska University in Lublin (1988, Faculty of Mathematics, Physics and Chemistry). Received her Ph.D. degree in 1996 in physical chemistry from UMCS. She works in the Department of Interfacial Phenomena in the Faculty of UMCS. Her research work is largely concentrated on physicochemistry of the surface and interface phenomena. She is a co-author of 63 publications.