HIGHLY ACTIVE CARBONS ON BASE OF BIOMASS WASTE - NUT SHELLS

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Abstract. The research is devoted to obtaining of highly porous activated carbons from apricot stones and pistachio, hazelnut, walnut shells from various regions using thermocatalytic activation with sodium hydroxide. Influence of the raw material properties and origin, as well as the precursor to activator ratio on a porous structure was studied. It was found that at activation temperature 700 ºC and NaOH to carbonizate ration 2:1 and 3:1 a highly developed porous structure is being formed, which can be controlled altering meso- and micropores volumes. It is demonstrated that the highest porosity was achieved in the case of walnut shells and apricot stones, and the obtained materials can be used for sorption and as electrodes in supercapacitors, fuel cells and Li-ion batteries

Keywords: nut shells; activated carbons; porosity; pyrolysis

Introduction

Currently biomass attracts widespread attention worldwide. This can be explained, firstly, by the drive to find alternative renewable sources of organic precursors, as well as the interest towards phytotherapy.

Horticulture is an important food source and the main source of income in piedmont and mountain regions in many developing countries, including cultivation of nut and stone fruits for provisions and biologically active compounds.

It is known that kernels of many nuts, such as walnuts, pistachios and hazelnuts, are highly valuable food products, which have caloric values, nutritiousness and absorbency surpassing meats, bread, eggs, cow milk and other foods [1]. When nut kernels are processed for oils, wastes, comprising shells, amount to 40-55 % from the nut weight. The main way of utilization of these wastes is burning them as fuel in furnaces alongside with other carbon-containing materials (Figure 1).

At the same time nut shells, as well as fruit stones, such as apricot, peach or cherry, have specific chemical-physical properties and can be used as highly valuable lignocellulosic precursors for production of carbonaceous sorbents [2-4]. Rational approaches to the processing of low-cost wastes improve the production feasibility and solve the utilization problems.
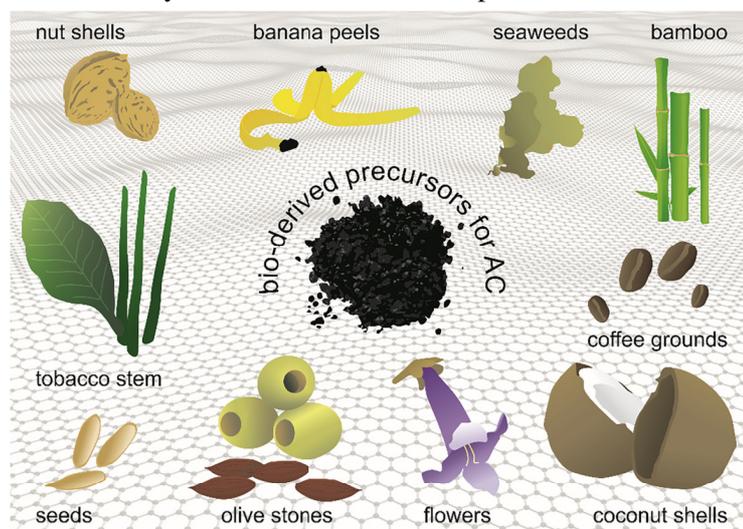

Fig. 1. **Biomass-derived activated carbon precursors [5]**

The main ways of carbonaceous sorbent application are within the framework of technological processes adsorption based purification, separation, extraction and concentration in gas and liquid media. The role of carbon sorbents constantly increases in the ecological problem solving, such as

drinking water and sewage purification, industrial exhaust gas sorption in energetics. Other areas of carbonaceous sorbent application are medicine and pharmaceutics as hemosorbents and enterosorbents. Lately carbonaceous nanomaterials are being applied as electrodes in supercapacitors and as oxygen reduction catalysts in fuel cells [6-8].

Properties of carbonaceous materials mostly depend on the chemical properties of activators, since activation processes define various pathways of precursor transformation, which leads to formation of materials with different structures and properties. Alkali, such as KOH or NaOH, are among the most effective activation agents, and allow obtaining of microporous sorbents with the specific surface more than 2000 $m^2 \cdot g^{-1}$. These materials are currently widely studied, since control of the pyrolysis condition can lead to formation of activated carbons with the needed properties of nanoporous structures [9-11]. Alkali hydroxides interaction with the precursors takes place already at room temperature [12].

Thermally initiated reactions of the precursor with MeOH (where $Me = K^+$ or Na^+) are responsible for the three main processes:

1. formation of metal containing surface complexes,
2. their conversion into carbonates and oxides (mainly Me_2CO_3 and Me_2O) in reactions with the edge C atoms of the graphene plains,
3. Me_2CO_3 and Me_2O reduction into metals.

Metal oxide reduction and bonding with carbon are two main factors, which provide formation and development of the porous structure [9]. If the process takes place in the optimal conditions (activator KOH or NaOH, 700-900 ºC, 1-3 hours), then the type of material (biomass, coal, etc.) does not influence the process anymore. The development of the porous structure directly depends on the presence of oxygen in the surface functional groups of the precursor [13]. It should be noted, that porosity of activated carbons is highly dependent on the ratio MeOH/precursor and the type of hydroxide. Without the alkali addition, it is practically impossible to obtain highly porous carbonaceous sorbents with developed nanoporosity [12; 14].

Experiment

Materials: pistachio shells (*Pistacia*) (Uzbekistan – **Puz**, USA – **Pus**); hazelnut shells (*Corylus avellana*) (Latvia – **Cor**); walnut shells (*Júglans régia*) (Uzbekistan – **Jug**); apricot stones (*Prunus armeniaca*) (Uzbekistan – **Pr**). The elemental composition and ash content of the samples is shown in Table 1.

Table 1

Elemental analysis of the samples under study

Samples	N, %	C, %	H, %	O, %	Ash content, %
Puz	0.46	49.66	4.45	45.42	0.31
Pus	0.21	47.59	4.61	47.58	0.71
Cor	0.28	51.05	4.51	44.16	0.99
Pr	0.18	50.44	4.46	44.92	0.24
Jug	0.23	50.90	4.74	44.14	0.81

Carbonization was performed in a Nabertherm 40 l muffle oven, Lilenthal, Germany. Heating rate 10 ºC min^{-1} up to 500 ºC, duration at max temperature 2 h. Carbonizates were refined using a planetary mill Fritsch Pulverizette Classic 4. For the activation fraction 10 μm were used.

Activation is schematically illustrated in Fig. 2 – it comprises two stages of thermal treatment. Carbonized material was impregnated with 50 % water solution of NaOH in mass ratios of dry alkali to carbonizate 2:1 and 3:1. The mixture was activated at 700 ºC for 120 min. The pyrolysis product was washed with deionized water, hydrochloric acid and water again to achieve the filtrate pH 5. Activated carbons were dried at 105 ºC overnight. The ash content in the samples was 0.1-0.5 %.

The porous structure of the AC was evaluated from N$_2$ sorption/desorption isotherms determined in a sorptometer Quntachrome NOVA 4200e (Boynton Beach, FL, USA). Degassing was performed at 300 ºC for 2 h. The results were assessed using Quantachrome software and are based on the theories

by Brunauer-Emmet-Teller (BET, in p/p0 range 0.05–0.35), Dubinin-Radushkevich (DR, in p/p0 range 10^{-5} – 0.35), and the density functional theory (DFT, in whole p/p0 range).
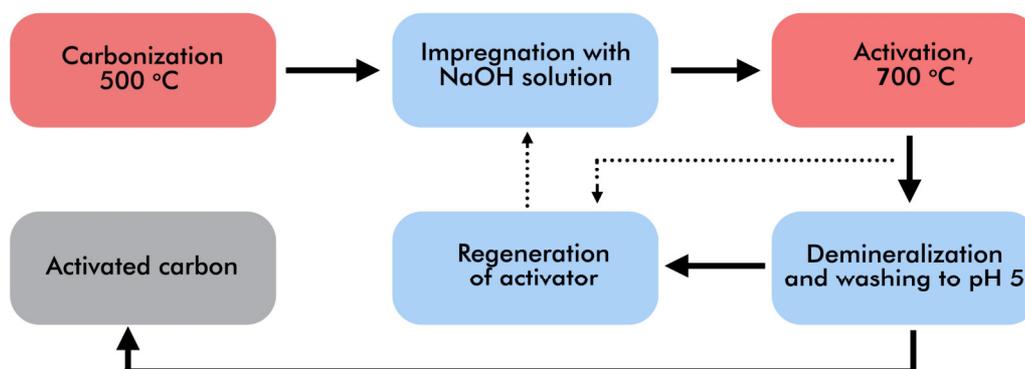

Fig. 2. **Schematic representation of microporous carbon material synthesis**

All experiments were made at least in quadruples and the experimental error was within 5 %.

Results and discussion

According to the elemental analysis (Table 1) the nut shells and apricot stones under study have a similar composition. The highest content of carbon, above 50 %, alongside with the lowest content of oxygen, was observed in the case of hazelnut and walnut shells, as well as apricot stones.

To obtain activated carbons on the base of various nut shells and apricot stones, precursors were carbonized and then refined. According to the thermal analysis data, the main part of organics of all samples under study is being removed in the temperature range 400-500 ℃ [15], thus the carbonization temperature was 500 ℃. Carbonizate yields altered negligibly in the range from 28.6 to 31.4 % despite the different origin of precursors (Table 2). At the first stage of thermal treatment, namely carbonization, the framework of future active is being formed – the initial porosity.

Then the carbonizates were impregnated with the water solution of NaOH and subjected to thermochemical activation at 700 ℃ for 2h. The ratios of dry activator matter to carbonizate were 2 and 3 to 1. At the second stage, the main reaction is the following [12; 16]:

$$6NaOH + 2C = 2Na + 3H_2 + 2Na_2CO_3$$

The yield of activated carbons from the carbonizate at the ratio of activator to raw material 2:1 was more than 40 %, and when the ratio was 3:1, the yield decreased for 5-8 % (Table 2). According to the results of nitrogen sorption, it was found that all the obtained activated carbon samples have a highly developed porous structure, which is characteristic to the highly active sorbents (Figure 3). Judging from the isotherm slopes, all of the samples are microporous.

At the activator to carbonizate ratio 2:1, maximum specific surface parameters (S_{BET}) were observed in the case of walnut shells (Jug) and apricot stones (Pr) – more than 2200 $m^2 \cdot g^{-1}$ (Table 2). The samples of active carbons based on hazelnut (Cor) and Uzbekistan pistachio (Puz) shells had a lower specific surface (above 1800 $m^2 \cdot g^{-1}$).

Table 2

**Ash content of samples and yield of carbonizates and activated carbons**

| Samples	Carbonizate yield, %	Yield of activated carbon from the carbonizate, %		Specific surface, $m^2 \cdot g^{-1}$	
		NaOH to carbonizate			
		2:1	3:1	2:1	3:1
Puz	28.6	43.0	38.8	1876	2395
Pus	30.6	41.0	35.6	2148	2773
Cor	30.7	44.0	35.8	1816	2171
Pr	31.4	41.3	34.1	2223	2977
Jug	29.9	42.0	36.0	2230	2982
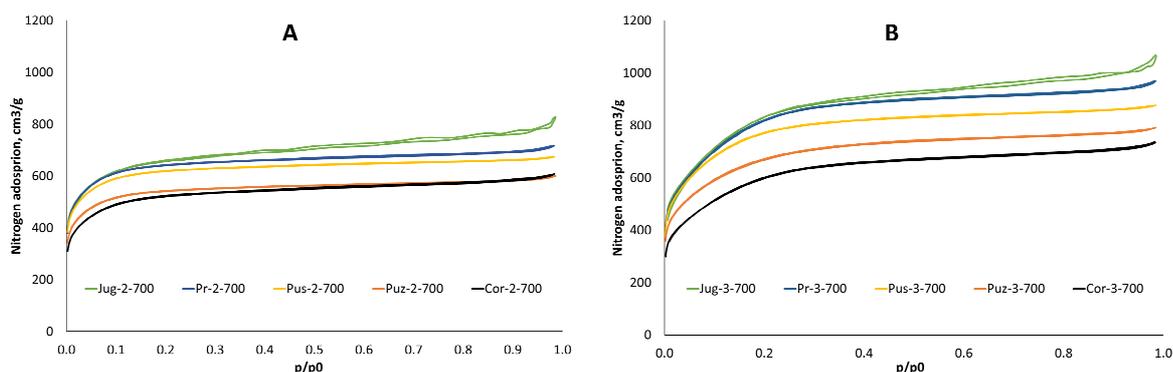
Fig. 3. **Isotherms of nitrogen sorption and desorption at 77K by the activated carbons on the base of nut shells and apricot stones:** A – 2:1 NaOH to carbonizate ratio; B – 3:1 NaOH to carbonizate ratio

Porosity of the samples increases with the increase of the activator to carbonizate ratio from 2 to 3:1 (Figure 3). Not only the BET specific surface increases, which in case of Jug and Pr surpasses the theoretical possible and is more than 2900 $m^2 \cdot g^{-1}$, but also the average pore size and the total pore volume, which reaches values more than 1.5 $m^3 \cdot g^{-1}$ (Figures 3, 4, 5).
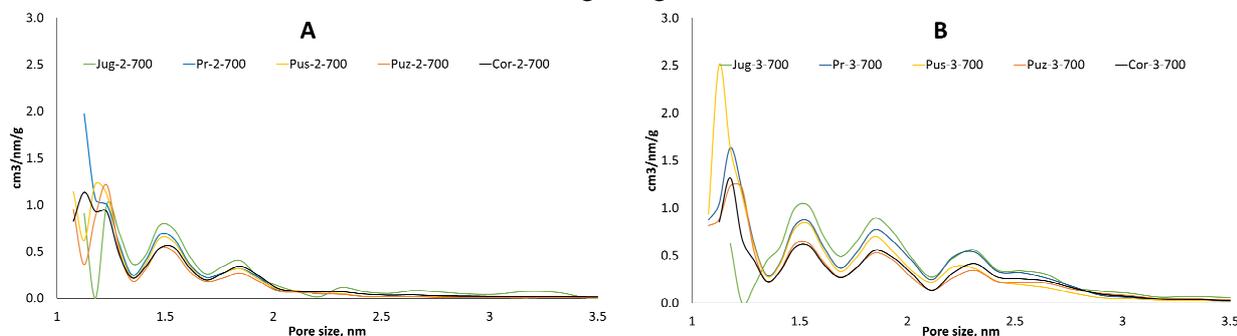
Fig. 4. **Pore size distribution of the activated carbons on the base of nut shells and apricot stones:** A – 2:1 NaOH to carbonizate ratio; B – 3:1 NaOH to carbonizate ratio

With the increase of the activator ratio also the volume of mesopores with sizes 2-3 nm increases (Figures 3 and 4). The alteration of the porous structure is also supported by the presence of hysteresis on the isotherms, which points at capillary condensation phenomena in the process of nitrogen sorption. This can enhance the area of application of these sorbents, particularly in sorption of liquids.
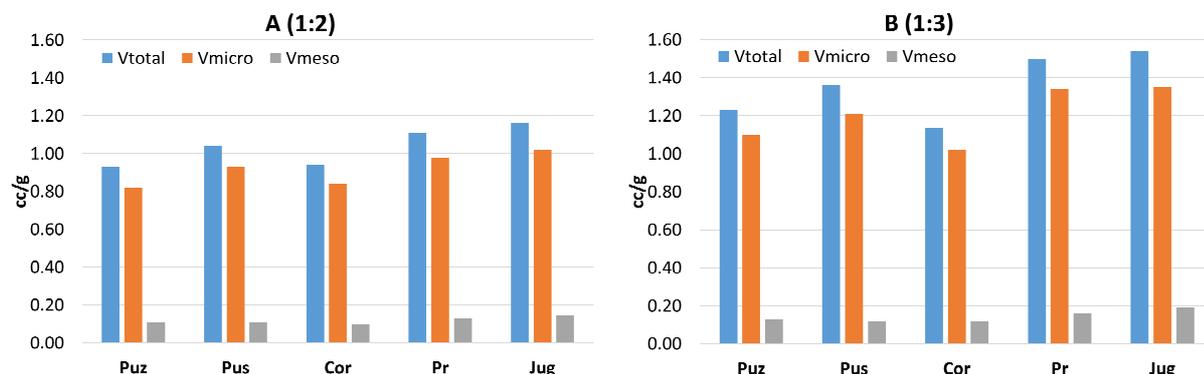
Fig. 5. **Total volume and ratio of micro- and mesopores of the activated carbons on the base of nut shells and apricot stones:** A – 2:1 NaOH to carbonizate ratio; B - 3:1 NaOH to carbonizate ratio

The obtained nanoporous sorbents on the base of nut shells and apricot stones, as well as other types of plant biomass, can be widely applied not only for sorption, but also for energy accumulation and transfer – as electrodes in supercapacitors, fuel cells and Li-ion batteries [6; 17].

Conclusions

Highly active nanoporous carbons on the base of carbonizates of nut shells and apricot stones were obtained using alkali thermochemical activation with NaOH. It was found that at the activation temperature 700 °C and NaOH to carbonizate ration 2:1 and 3:1, a highly developed porous structure is being formed, which can be controlled altering meso- and micropores volumes. It is demonstrated that the highest porosity was achieved in the case of walnut shells and apricot stones, with the BET specific surface surpassing the theoretical possible, more than 2900 $m^2 \cdot g^{-1}$, and the total pore volume more than 1.5 $m^3 \cdot g^{-1}$. The incredibly high porosity of the obtained activated carbons blazes the avenue for the widest spectrum of their applications.

Acknowledgements

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