Synthesis of Carbonized Nano Mesoporous Sorbents Based on Vegetable Raw Materials

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Abstract This article presents the results of the synthesis of carbon nanomaterials: Nanoscale materials obtained by carbonization of waste agricultural products (apricot kernel, walnut, rice husk). The results of physico-chemical characteristics of the obtained nanomaterials. Physico-chemical parameters of the synthesis of carbonized sorbents based on plant raw material are investigated along with the properties of these sorbents. The data of FTIR, ESR spectroscopy & BET- method, as well as electron microscopy are reported. It is stated that carbonized sorbents possess high specific surface area and porosity. Carboxylic, carbonyl, hydroxyl groups are detected on the surface of the synthesized sorbents. It is assumed that high sorption ability with respect to Co, Ni, Pb, Cd, Cu ions is connected with the formation of chelate complexes. It was shown that carbonized nanostructured sorbents are able to: adsorb cesium-137 (^{137}Cs), strontium-90 (^{90}Sr) & lead-210 (^{210}Pb) successfully; reduce ions of gold (III) on the surface selectively; separate fusococcine and similar biostimulators effectively; remove LPS-endotoxines from blood plasma selectively. They may be used as carriers to introduce probiotics into intestine thanks to formation of stable colonies on their developed surface. A method of preparation of honeycomb monoliths from carbonized rice husk with developed mesoporous structure via modification of the porous structure by silica leaching has been developed.

Keywords Nanotechnology, Nanomaterials, Carbonization, Electron Microscopy, Carbon Materials, Synthesis, Adsorbents

processes of purification from harmful contaminants, recovery of valuable substances from liquid and gaseous media, in medicine to clean the blood from the endo-and exotoxins, for detoxification of the gastro-intestinal tract and other purposes. The Institute of Combustion Problems, studies on the development of nanostructured sorbents, as well as the raw material used by waste rice husks, apricot, grape seed and walnut shells.

The aim of this study was to develop such sorbents, which would be characterized by high mechanical strength and withstand high pressures, which have large capacity and high wear resistance, enabling them to work for a long time. And also it was necessary to investigate the applicability of nanostructured carbon sorbents for the separation of biomolecules. In accordance with the objective addressed the following specific objectives: obtaining and testing of nanostructured carbon sorbent for the molecular-sieve chromatography of markers and testing of nanostructured carbon sorbent for the separation of protein-lipid complex, and plant bio-stimulator.

Industrial adsorbents based on activated carbons obtained from different types of organic materials: stone, brown coal, hard coal, peat, wood and its products, materials of animal origin. Non-traditional raw materials, which have not yet found wide application in industry, can be of various bones of fruit trees (apricot, peach, plum, cherry), grape seed and walnut shells, which are currently waste products.[2]

The need for low-cost sorbents that meet the requirements of production (a good sorption capacity, adjustable size and pore structure, etc.) leads to the development of new methods of obtaining sorbents. Activated carbon from plant material is cheap and readily available sorbent with a high porosity, strength, and reusable.

Processing of this type of stuff is usually performed in an oxygen-free environment in a vacuum or under nitrogen, at temperatures that are in the range from 150 to 900 °C. The duration of isothermal holding at final temperature of pyrolysis ranges from 10-90 minutes. Analysis of the literature allows us to conclude that the temperature of pyrolysis of different types of plant materials are similar. In all cases, the output carbonizate decreases with increasing temperature, with most weight loss occurs in the range

1. Introduction

Carbon adsorbents are widely used in various processes of purification of contaminants and recovery of valuable materials from liquids and gases. Increasingly, they are used in medicine, for example, to remove from the body fluids of individual components for cleaning the blood, as well as for the chromatographic separation of biomolecules[1].

Recently, carbon sorbents are widely used in various

150-500°C. At the same time in the solid residues increases the carbon content, which at temperatures above 750°C higher than 90%. Complete carbonation typically occurs at 850-900 °C[3-4].

The mechanism of progressive activation of plant carbonize probably lies in the enlargement of pores of all types and the transformation of ultra micropor in the micropores, some fraction of micropores in supermicropor and mesopores, and mesopore large in the macropores. Since the content of ultra micropor carbonized high enough, the micropore volume increases with the degree of activation of at least 40-50% of ablation, and further because of these reasons is reduced. With regard to the specific surface area, calculated on the adsorption of CO₂, then the appearance of large micro pores and supermicropor this adsorption proceeds by a mechanism not only to their bulk, and surface filling. Increasing ablation leads to a significant increase, both the volume and the effective pore radius.

In the production of activated carbons the main stages of the recycling process of the carbon material of plant origin are the " carbonation + activation " they provide the necessary formation of structural and physicochemical properties of the target products. The aim of this work is the selection of optimum conditions of carbonization and the study of the structure of obtained adsorbents. [5].

2. Experimental

2.1. Synthesis of Carbonated Nanoscale Mesoporous Materials

The process of carbonization of the samples was carried out under isothermal conditions. Inoculation of samples was performed in a rotating reactor, an inert atmosphere at a temperature of 100-900°C, the argon flow rate 50 cm³/min, contact time 60 min. For the experiment took powdered fraction (d = 2 mm, 4 mm) and placed into the reactor.

2.2. Study of Physico-Chemical Characteristics of Nanomaterials

The most important and reliable information about the structure of the carbonized carbon material can provide scanning electron microscopy. Scanning electron microscopy images of samples were obtained carbon material carbonized at different temperatures. Pictures carbonized samples are shown in Figures1 and 3.

Figure 1. Electron micrograph of the surface of the particles apricot kernel before carbonization (scale 1:3000)

Before carbonization apricot kernel are undeveloped and very dense structure, has been a small amount of a diameter of 780 nm to 3000 nm, as shown in Figure 2.

Found that the carbonization temperature 800°C where there is a significant loosening of the appearance of numerous pores larger than 200 nm. Thus, a study produced the following results. Figure 2a presented a snapshot of the entire surface of the particles of carbonized apricot pits at 800°C. For the analysis of samples were collected, dispersed up to 1 mm. The general form of the particles is shown in Figure 2b. As can be seen from this figure, the particles have a porous structure. Then, the depth of electron-microscopic study of the structure of the material carbonized at a temperature of 800°C, under high magnification.

a

b

Figure 2. Electron micrograph of the surface of particles of carbonized samples with 800°C

Figure 3. Electron micrograph of the sample carbonized at a temperature 800°C (scale 1:1100)

Table 1. Specific surface area, porosity and density of the carbonized sorbent on the basis of rice husk and apricot kernel

Temperatures Carbonation °C	Density, g/cm ³		Porosity, cm ³ / g		The specific surface area, m ² / g	
	rice husk	apricot kernel	rice husk	apricot kernel	rice husk	apricot kernel
The initial samples	1,58	1,74	0,19	0,21	238	240
400	1,41	1,43	0,86	0,95	281	350
450	1,21	0,92	1,02	0,98	456	560
500	0,96	0,86	1,28	1,28	532	770
550	0,76	0,61	1,56	1,39	673	780
600	0,55	0,58	1,91	1,85	807	810
650	0,46	0,50	2,16	1,86	910	815
700	0,39	0,49	1,96	1,90	758	800
750	0,36	0,47	0,95	1,87	684	810
800	0,34	0,45	0,97	2.10	630	830

With an increase up to 1100 times, you can see that on the surface of the sample contains large pores of 1500 nm to 3000 nm and on the borders of large pores are visible double-porous membrane (Figure 3a). It was interesting to examine the inner surface of large pores (Figure 3b). As seen in the micrographs, with a stronger increase of the inner surface of large pores are present pores ranging in size from 200 nm to 1300 nm.

Thus, by using electron microscopy revealed that the carbon material, carbonized at a temperature 800°C is the most well-developed structure and porosity, and appearing at this temperature, carbon nanotubes attached to beads carbon material high strength and increase the specific surface area.

Figure 4 shows a nonlinear increase of the carbon concentration in the case of WB samples. This means that with the temperature rise the carbonization runs through different stages. At comparatively low heating temperatures, a pyrolytic removal of water mainly takes place, but at higher temperatures, a removal of low-molecular-weight carboniferous products and various tars takes place.

Figure 4. Dependence of carbon content on carbonization temperature

2.3. Determination of Specific Surface Area, Porosity and Density of the Carbonized Material

The specific surface area of the carbonized sorbent was studied by thermal desorption of argon. Table 1 shows the results of the specific surface area, porosity and density of

the carbonized samples apricot kernel and rice husk. The highest specific surface area ($910 \text{ m}^2 / \text{g}$) sorbent has received at 650°C . Further, when the temperature decreases the surface area of $758 \text{ m}^2 / \text{g}$ (rice husk, carbonized at a temperature 700°C) to $630 \text{ m}^2 / \text{g}$ (rice husk, carbonized at a temperature 800°C). If the initial density is rice husk - 1.58 g/cm^3 , for rice husk, carbonized at a temperature 400°C , the figure is - 1.41 g/cm^3 , and then the samples carbonized at a temperature 800°C , reduced to a value of 0.34 g/cm^3 . In this case the porosity is increased. Thus, in the initial porosity is rice husk - $0.19 \text{ cm}^3 / \text{g}$, then with increasing carbonization temperature up to 400°C , this index increased 4.5-fold ($0.86 \text{ cm}^3 / \text{g}$), and carbonized at a temperature of sorbent 800°C , this figure is - $0.97 \text{ cm}^3 / \text{g}$. The density of the initial samples, based on the apricot kernel, is - 1.74 g/cm^3 , with increasing carbonization temperature decreases the density of the sorbent in a 4 - fold, and at a temperature carbonization 800°C , and the figure is - 0.45% . Comparison of the porosity of the initial and carbonized at a temperature of sample apricot kernel 600°C shows that in the initial sample porosity is - $0.21 \text{ cm}^3 / \text{g}$, and the samples carbonized at a temperature 600°C - $2.10 \text{ cm}^3/\text{g}$. With further carbonization apricot kernel, porosity decreases, and the samples carbonized at a temperature 800°C , the figure is - $1.84 \text{ cm}^3/\text{g}$. The specific surface area of the original apricot kernel $240 \text{ m}^2/\text{g}$, and with increasing temperature carbonization can see an increase in specific surface area of carbonized samples.

From these results, it became known that the maximum values of porosity and density of the samples shows rice husk, carbonized at a temperature of 650°C as well. apricot kernel samples, carbonized at a temperature 800°C

Thus, according to the results of the experiments found that the carbonization of the samples apricot kernel and rice husk, increases the specific surface area, porosity and a decrease in the density of the final product.

3. Conclusion

The results by electron microscopy revealed that the carbon material, carbonized at a temperature 800°C is the most well-developed structure and porosity, and appearing at this temperature, carbon nanotubes attached to beads carbon materials high strength and increase the specific surface area.

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