

THE INVESTIGATION OF THE POROUS STRUCTURE OF CARBON SORBENTS BASED ON β -CYCLODEXTRIN FOR USE IN ENVIRONMENTAL PROTECTION TECHNOLOGIES

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Abstract. In this paper, the porous structure of three types of β -cyclodextrin (β -CD) carbons was synthesized and investigated. The first carbon was obtained from pure β -CD, the second carbon was synthesized from β -CD using the KOH activator, and the third carbon was synthesized from pure β -CD with additional ultrasonic treatment in the non-cavitation mode at the last stage. It was found that the carbon from pure β -CD has a micromesoporous structure with a small specific surface area (~ 35 m²/g). Activation with KOH causes a significant increase in the specific surface area (~ 654 m²/g) due to an increase in the content of micropores with an average size of 1.25 nm. The ultrasonic treatment causes mechanical grinding and oxidation of the carbon surface. It has been shown that such treatment increases the mesopore content and significantly changes the mesopore size distribution. It has been established that the oxidation of the β -CD carbon surface after ultrasonic treatment causes an increase in its hydrophilicity of up to 83.1 %. The increase in hydrophilicity will allow more efficient use of synthesized carbon and composites based on it in solving the problems of environmental safety in water environments.

Keywords: activated carbon, β -cyclodextrin, adsorption/desorption isotherm, specific surface, pore volume, pore size distribution, hydrophilicity.

1. Introduction

The technological development of human society and effective innovative developments are

rapidly changing the world around us. This primarily concerns the technology of computerized devices and microprocessor technology, energy and signal conversion, the production of nanomaterials, biotechnological and biomedical equipment. All these achievements have been made possible by the development of nanoscience and nanotechnology, which operate on nanostructured materials that have unique properties compared to their macroscopic analogues. On the other hand, such technological progress causes additional types of pollution and increased energy consumption, which has become a global challenge for humanity. In order to solve these problems, functional systems and high-performance materials are needed, the production of which will be accompanied by low levels of harmful emissions, and these systems and materials will be characterized as environmentally friendly (Larcher, Tarascon, 2015; Yamaguchi, Itami, 2017). An important aspect is not only the composition of materials but also the control of their structural properties. Scientific research on such nanomaterials can provide effective solutions to many environmental problems (Vance et al., 2015; Ariga et al., 2018; Almeida et al., 2020).

Nanotechnology includes a wide range of scientific and technological approaches united by the goal of synthesizing and studying the properties of objects with nanometer dimensions. The knowledge gained over the past decades in this area is gradually being integrated into the creation of functional systems

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and materials based on the achievements of another modern science, supramolecular chemistry. The interdisciplinary merger of these sciences created a new scientific concept – nanoarchitectonics (Ariga et al., 2018; Ariga, 2021). The basis of this concept is the idea of creating functional materials from atoms, molecules, and nanoscale elements by manipulating them on the atomic/molecular level, modifying single molecules using chemical procedures, fabricating nano- or microstructures through supramolecular self-assembly/self-organization and structural rearrangement under the influence of external forces and influences (Ariga et al., 2011). Nanoscale blocks, such as host-guest complexes, are often used to synthesize such materials. The most suitable host materials are layered compounds and micro- or mesoporous matrices. Such matrices can be either mesoporous structures based on silica (SBA-15, MCM-41, KIT-5, etc.) (Mane et al, 2012; Chabecki, 2022; Maksymych et al, 2023) or carbon porous materials (Hu et al., 2012; Gu, Yushin, 2013). The advantage of carbon materials is the ability to obtain them with a defined porous structure and a modified surface with appropriate functional groups. The main carbon materials are most often carbon nanotubes, graphene, and activated carbon (AC). However, the high cost of carbon nanotubes and

graphene hinders their widespread use in various applications. Therefore, AC has significant advantages due to easy access to raw materials and fairly simple methods of synthesis by activation/carbonization. However, the following question arises: can any AC be used to create stable host-guest complexes? Research by Shvets et al (2014) has shown that most precursors for the synthesis of ACs have a structure that cannot accommodate certain dopants in their internal microstructure, which would regulate, for example, the electronic structure of the resulting nanoporous carbon material and create stable host-guest complexes at the carbonization stage.

Among the host materials that can form stable supramolecular host-guest complexes with various organic, inorganic, and biological molecules (“guests”) are cyclodextrins (Yoshida et al., 1999; He et al., 2008). Cyclodextrins (CDs) are cyclic glucose oligomers obtained enzymatically from starch, i.e., they are materials of organic origin. CDs are composed of D-(+)-glucopyranose residues linked to polypropylene glycol by α -D-1,4-glycosidic bonds. CDs are distinguished by the number of glucose residues contained in one molecule: α -CD consists of 6 glucopyranose units, β -CD contains 7 units, and γ -CD contains 8 units.

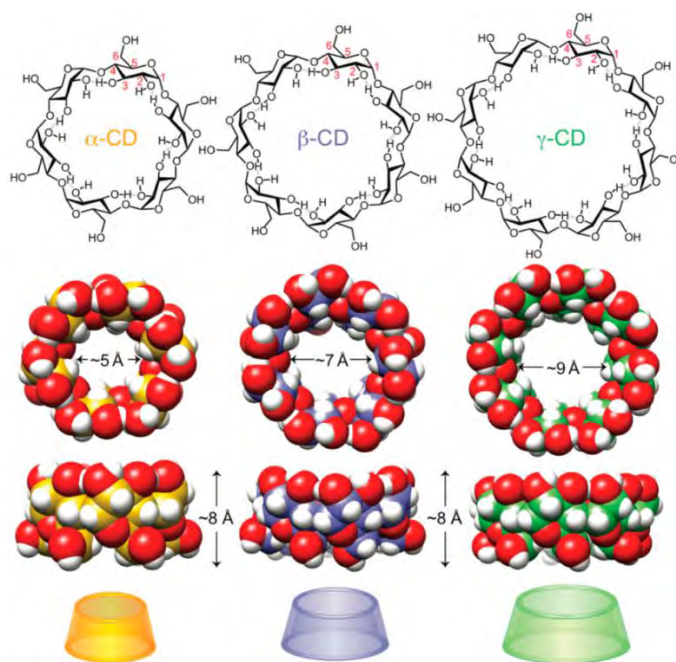


Fig. 1. Molecules of α -, β - and γ -cyclodextrins (Bruns, 2019)

The shape of CDs molecules can be described as a truncated cone with a cavity in the middle. The general view of CDs molecules and their corresponding models is shown in Fig. 1. As can be seen from Fig. 1, all OH groups in CDs molecules are located on the

external surface. As a result, the internal cavity of the CDs is hydrophobic, and the external cavity is hydrophilic. Due to the unique distribution of hydrophilic and hydrophobic groups, β -CD has the greatest practical interest. The molecules of this CD

have the ability to reversibly and selectively bind organic, inorganic, and biological molecules, forming stable host-guest complexes (Thatiparti et al., 2010; Chen, Jiang, 2011; Zhang et al., 2013; Hu et al, 2014). Since the cavities of individual β -CD molecules are open on both sides, the guest molecules can be inserted into the β -CD ring from both sides. The high density of electronic states inside the cavity facilitates the capture of electrons from the “guest” molecules. This leads to a change in the spectral properties of both the molecules in the cavity and the β -CD molecules themselves. If carbonization of such supramolecular complexes occurs, the electronic structure of the resulting nanoporous carbon material can be adjusted to a certain extent, depending on the type of dopants.

Grygorchak et al (2019) noted that α -modification is unstable. The study of carbon materials synthesised from β -CD and γ -CD for electric charge storage is described in (Grygorchak et al., 2018; Jeong et al., 2020). It was found that, independently of the type of “guest” material, the best energy parameters were obtained using β -CD. However, the studied carbon materials were synthesized from already-formed supramolecular complexes and contained guest molecules. There are practically no studies of carbon materials obtained from pure β -CD in the literature. Also, very few studies have been devoted to determining the effect of various activators or treatments on the properties of carbon materials synthesised from β -CD (Grygorchak et al., 2018; Zhong et al., 2021). For environmental technologies, the parameters of the porous structure are crucial for carbon materials, so the aim of this study was to investigate these parameters in carbon materials synthesised from pure β -CD, with additional activation of KOH and with additional ultrasonic (US) treatment.

2. Experimental part

2.1. Synthesis of materials

For the synthesis of AC, β -CD from Aldrich Chemical Co. (USA) was used. All cyclodextrins have the feature of strong foaming when heated. This is due to dehydration and the intensive emission of carbon dioxide. As a result, the volume increases many times over. Such processes require pyrolysis in several stages. In the first stage, β -CD was kept at 500 °C for 5 hours in a reactor with a flowing inert atmosphere (argon). After cooling to room temperature, the resulting carbonisate was mechanically ground, and the second stage was carried out. At the second stage, it was kept at 800 °C for 4 hours, also in a reactor with flowing argon. The carbonized carbonaceous material

with β -CD obtained in this way was washed with hot distilled water. The washed carbonisate was dried at 100 °C to a constant weight.

To investigate the effect of alkaline activation, the dried carbonaceous material was mixed with a saturated aqueous KOH solution in a mass ratio of carbon: KOH = 1:3. After mixing, the resulting mixture was dried to a constant weight in an oven at 100 °C. The material was carbonized at 800 °C for 2 h in an argon atmosphere. The resulting AC was washed three times with hot distilled water and dried to a constant weight in an oven at 100 °C.

One of the perspective reagent-free methods of controlled modification of AC for its use in solving various applied problems is US treatment in the liquid phase (Bordun et al., 2014; Balaban et al., 2014; Ptashnyk et al., 2020). To investigate the effect of US radiation in the non-cavitation mode, the AC was treated in a spherical reactor. During the treatment, the AC was in the reactor in the form of a 15–20 wt. % dispersion in distilled water. The frequency of US radiation was 22 kHz, and the treatment duration was 10 min. The resulting AC was washed and dried to a constant weight in an oven at 100 °C.

2.2. Methods of experimental research

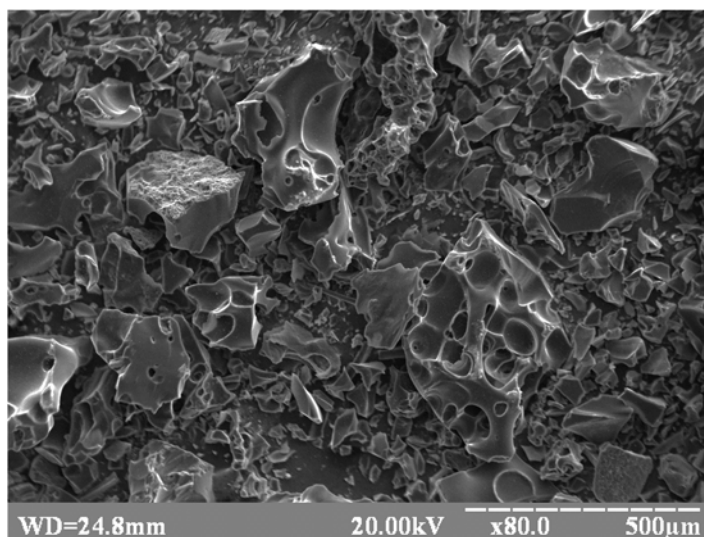
SEM images of the synthesised carbon were obtained using a scanning electron microscope with a low vacuum chamber and an energy dispersive microanalysis system REMMA-102-02.

The porous structure parameters of the investigated types of AC were determined by modeling the data of nitrogen adsorption/desorption isotherms at its boiling point. The isotherms were obtained using an automated analyzer Quantachrome Autosorb (Nova 2200e). The samples were pre-degassed in a vacuum at 453 K for 20 hours before the measurements.

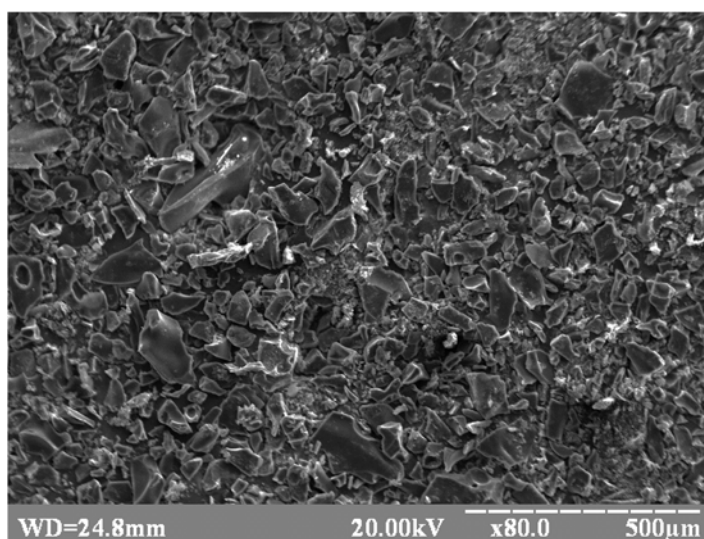
The total volume of pores accessible to the liquid was determined by soaking cylindrical tablets made of AC in heptane for 24 h. Heptane was chosen for its good wetting of the carbon surface. The proportion of hydrophilic pores was determined by the amount of water absorbed during soaking under similar conditions. The calculation of hydrophilic-hydrophobic properties was performed according to the method (Baranov et al., 1971).

3. Results and Discussion

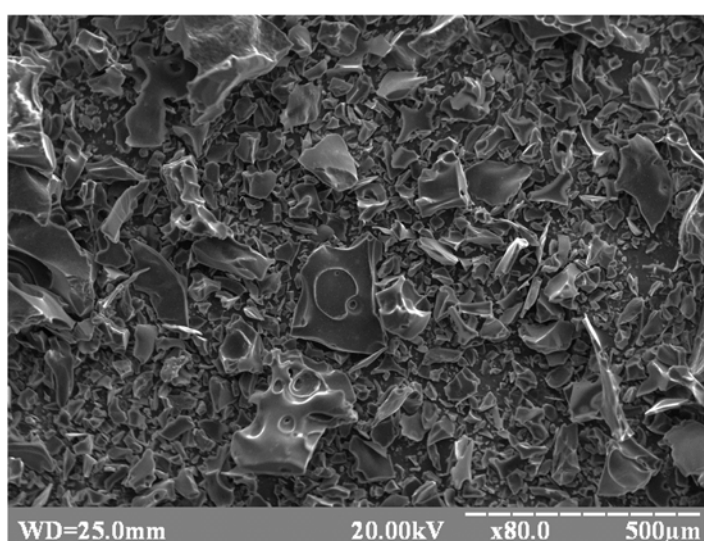
The obtained SEM images are shown in Fig. 2. As can be seen from Fig. 2, *a*), due to foaming during carbonization, a macroporous carbon structure with corresponding rounded cavities is obtained. The size of the carbon particles is in a wide range.



a



b



c

Fig. 2. SEM images of the investigated ACs from β -CD.
a – initial AC; b – AC after KOH modification; c – AC after US treatment

After additional KOH modification (Fig. 2, b), we observe a significant grinding of carbon particles and an almost complete absence of rounded cavities, which were characteristic of the initial carbon. In Fig. 2, c) for AC after US treatment, we have insignificant changes compared to the initial carbon. The carbon particles have become more crushed; there are fewer particles with rounded cavities, but the overall picture remains the same as in the initial carbon.

The nitrogen adsorption/desorption isotherms for the studied carbon materials are shown in Fig. 3.

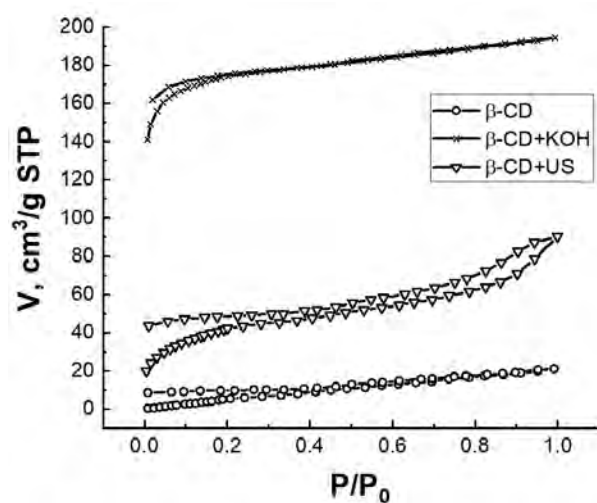


Fig. 3. Isotherms of nitrogen adsorption/desorption by the studied AC synthesized from β -CD.

The adsorption of nitrogen by the initial carbon from β -CD is rather insignificant, and the resulting isotherm is difficult to classify into any type. However, the general shape and magnitude of adsorption is characteristic of non-porous or low-porosity adsorbents. After the US treatment, the isotherm is located higher in the amount of adsorbed nitrogen, showing an increase in the specific surface area and volume, and can be characterised by its shape as a type II isotherm according to the IUPAC classification (Thommes et al., 2015). In addition, hysteresis is observed in the region of high relative pressures. The shape of the hysteresis can be determined as the H4 type. Hysteresis loops of type H4 are often found in aggregated zeolite crystals, some mesoporous zeolites and microporous carbon materials. The analysis of the amount of adsorbed nitrogen and the shape of the curve for AC from β -CD after KOH modification suggests that it belongs to type I according to the IUPAC classification. Such isotherms are characteristic of microporous solids with a relatively small external surface (some types of AC, molecular sieve zeolites

and some porous oxides). It should be noted that all isotherms are characterised by the divergence of the adsorption and desorption branches. This is especially evident in the low relative pressure region, which is why this behaviour is called low pressure hysteresis. It can be caused by various reasons. In our case, the most likely cause is the irreversible retention of adsorbate molecules in pores whose size is close to the size of the adsorbate molecules.

A more detailed quantitative analysis of the adsorption isotherms using various theoretical models provides confirmation or refutation of these assumptions and conclusions. To calculate the parameters of the porous structure of the investigated carbonaceous materials, the obtained isotherms were analyzed using the Quantachrome TouchWin software.

The Brunauer-Emmett-Teller (BET) multipoint method was used to determine the total specific surface area of the investigated AC (Rouquerol, 2014). This method approximates the experimental data with a linear dependence in the range of relative pressures $P/P_0 = 0.05 \div 0.35$ and calculates the specific surface area using classical relations. The Barret-Joyner-Halenda (BJH) method, which is based on the Kelvin equation, can be used to analyze the mesopore content of AC. The calculation of pore parameters (specific surface area of mesopores, mesopore volume, average mesopore radius) is most often performed using the desorption isotherm, which is closer to the true thermodynamic equilibrium (Rouquerol, 2014). Various modeling methods are used to analyze the microporous structure of ACs, including the MP-method, t-method, Dubinin-Radushkevich method (DR-method), DFT-method, etc. Since the shape of the isotherms indicates the presence of mesopores along with micropores, the t-method and DFT-method were used for the calculations. The essence of the t-method is to rebuild the initial adsorption isotherm in the range of relative pressures $P/P_0 = 0.2 \div 0.5$ as a function of a new variable t . The variable t is called the statistical adsorption thickness and is defined by the expression $t = \sigma W/W_m$, where $\sigma = 0.354$ nm is the monomolecular thickness of the nitrogen adsorption film. The DFT method was developed on the basis of density functional theory. It is based on quantum mechanical calculations using fundamental molecular parameters that characterize the gas-gas and gas-solid interactions in an adsorption system.

The results of calculating the porous structure parameters are given in Table 1, and Fig. 4 shows the distribution of micro- and mesopores by size.

Table 1

The porous structure parameters of ACs synthesized from β -CD

Sample AC	S_{BET} , m^2/g	S_{mezo} , m^2/g	S_{mikro} , m^2/g	S_{DFT} , m^2/g	V_{Σ} , cm^3/g	V_{mezo} , cm^3/g	V_{mikro} , cm^3/g	V_{DFT} , cm^3/g	$\langle d \rangle$, nm
β -CD	61.9	15.1	20.4	34.2	0.033	0.024	0.01	0.03	2.11
β -CD+KOH	654.3	23.1	600.7	599	0.301	0.035	0.247	0.27	1.84
β -CD+US	150.9	36.2	89.1	147	0.14	0.078	0.038	0.124	3.7

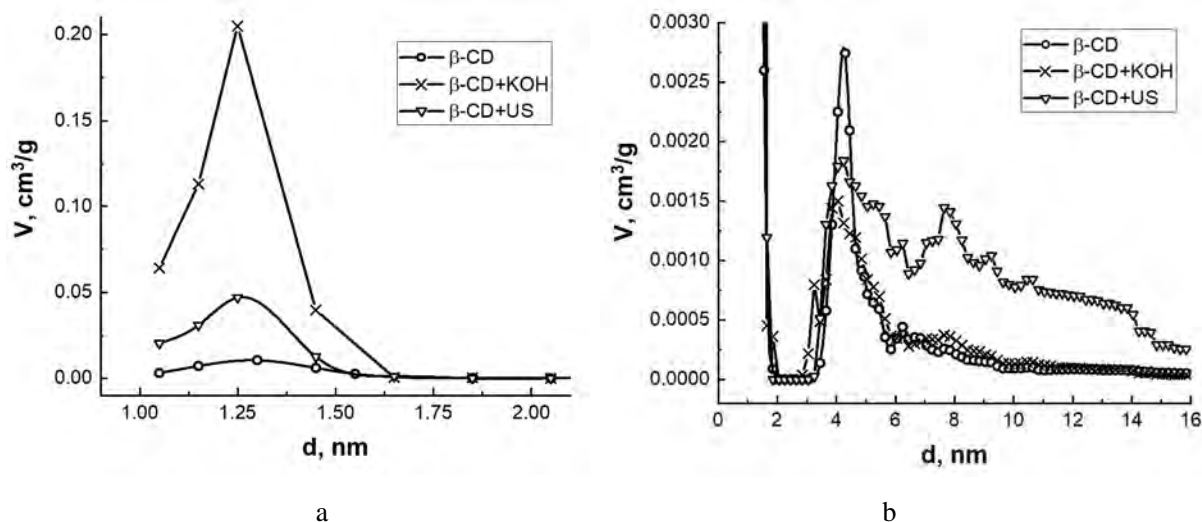


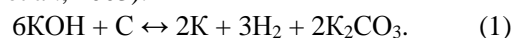
Fig. 4. The distributions of pore size for AC synthesized from β -CD
a – for micropores; b – for mesopores

As can be seen from Fig. 4 and the data in Table 1, the initial carbon from β -CD has almost the same specific surface area of mesopores and micropores. The result obtained by BET modeling is interesting. The obtained value of the specific surface area is almost twice as high as the data calculated by other methods. The reason for this may be both the limitations of the BET method and the surface features of the synthesised carbon, on which a monolayer of adsorbed nitrogen is formed. The porous structure of the initial β -CD carbon is determined by micropores with a maximum volume at a pore size of 1.3 nm and mesopores with a maximum volume at a pore size of 4.3 nm.

After additional treatment with KOH, we observed a significant increase in the specific surface area and porous volume. The data in Fig. 4 and Table 1 show that there is an intensive increase in the micropore content – the volume of micropores increases by almost 25 times. At the same time, Fig. 4 shows that the maximums in the pore distribution practically do not shift. As in the initial carbon, the porous structure is determined by micropores with a

maximum volume for pores with sizes of about 1.25 nm and mesopores with a maximum volume for pores with sizes of about 4.1 nm.

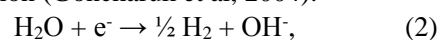
The cause of such a significant increase in the microporous volume is the active interaction of KOH with the carbon framework at high temperatures (Lillo-Ródenas et al., 2003):



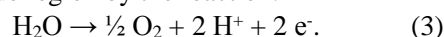
Additional US treatment in the non-cavitation mode caused a slight increase in the specific parameters of the porous structure. However, Fig. 4b shows that the mesopore size distribution changed significantly. There was an increase in the volume of mesopores in a wide range of pore sizes compared to the initial carbon. As a result, the average value of pore size $\langle d \rangle$ for carbon from β -CD after US treatment is the largest (Table 1).

In the non-cavitation mode of US exposure, oscillations of low intensity are observed, and the generated pressure does not exceed 100 kPa. In this case, the change in the porous structure occurs due to the appearance of secondary forces caused by convective transport and the interaction of particles in

the dispersed phase through collisions. In addition, the small nonlinearity of the functional dependence of the density and viscosity of the liquid on pressure has an additional effect (Mahamuni, Adewuyi, 2010). In the non-cavitation US regime, electrochemical processes can occur due to friction at the interface of liquid-solid or liquid-gas (Goncharuk et al., 2004). The cause of this is the relative movement of the phases of the water-carbon dispersed system. As a result of a certain duration of relaxation processes, local accumulation of charges of the same sign occurs, i. e., polarization of the double electric layer. With this polarisation, charges of the same sign on the surface of the dispersed phase relax more slowly than charges of the other sign in the solution. Therefore, the latter will have a greater influence on the final electrolysis products. Thus, the sign of the charges in the dispersed phase determines whether the electrolysis will be cathodic or anodic. The electrolysis of water in the cathode region follows the following reaction (Goncharuk et al, 2004):



and in the anode region by the reaction:



Thus, the non-cavitation mode of US treatment will have not only a mechanical effect on the AC particles, but also a chemical effect. To establish the mechanism of electrolysis, the pH of the water-carbon dispersion was measured before and after the US treatment. It was found that before the treatment, the pH was 8.32, and after the treatment, the pH was 7.71. Thus, ultrasound will cause the formation of oxygen and hydrogen ions by the anodic mechanism. This will cause additional oxidation of the AC surface. Since carbon is a non-polar substance, the oxidation of the surface of carbonaceous materials does not affect the adsorption of non-polar substances and their wettability on the carbon. In contrast, the adsorption of polar substances, such as water, is significantly affected by the presence of chemisorbed oxygen or oxygen-containing surface groups (Birkett, Do, 2006). The additional surface oxidation is confirmed by the change in hydrophilicity of AC from β -CD after the US treatment. Before treatment, the hydrophilicity was 56.7 %, and after treatment it increased to 83.1 %.

4. Conclusion

The investigation of the porous structure of the AC synthesised from β -CD showed that the obtained carbon has a small specific surface area. The porous structure has micropores with a maximum in the

distribution at 1.3 nm and mesopores with a maximum at 4.3 nm. For the application of composites and host-guest structures based on β -CD, it is necessary to use an additional chemical activation step. The use of potassium hydroxide KOH for this purpose made it possible to increase the specific surface area by almost 20 times and the total pore volume by almost 10 times. At the same time, this activator did not cause the appearance of pores of different sizes. The increase in pore space was due to an increase in the content of micropores, with a maximum volume for a pore size of 1.25 nm.

To be used in environmental technologies related to the purification of aqueous media, AC should have good hydrophilicity. The investigation of the effect of US treatment in the non-cavitation mode on carbon from β -CD showed that mechanical grinding of carbon particles and oxidation of its surface occurred. As a result, there is a slight increase in the pore space and a significant increase in the hydrophilicity of the AC.

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