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Advances in B(III) Removal by Adsorption on Nanoporous Carbon of Lignocellulosic Origin and Its Surface Modified Analogue

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By means of the traditional two-stage carbonization–activation process, a sample of nanoporous carbon was obtained from a dogwood seed as well as its analogue modified with salicylic acid. Porometric characteristics of carbons obtained are determined due to the N_2 sorption–desorption isotherms. As established, the prepared carbons have well-developed porous structure with a high specific surface area $S_{BET} = 1450 \text{ m}^2/\text{g}$, specific surface of mesopores $S_{me} = 350 \text{ m}^2/\text{g}$, and total pore volume $V_{\Sigma} = 0.7 \text{ cm}^3/\text{g}$. An assumption is made about the possibility of using such sorption materials for cleaning water sources from B(III) ions. For both samples, sorption studies are carried out for the absorption of boron from aqueous solutions. The sorption capacity of activated and additionally salicylic-acid-modified carbons with respect to boron ions as microimpurities contained in natural waters is studied. As shown, the modified carbon exhibits the maximum sorption properties, the adsorption capacity of which reaches 18 mg/g. An assumption is made about the mechanism of sorption of boron ions. In heterogeneous systems, the presence of oxygen-containing functional groups is demonstrated to be very effective in processes connected with removal of boron pollutants. The borate ion attacks the hydroxyl groups of the phenolic ring and forms a co-ordination bond between the boron atom in the borate ion and the oxygen atom in the hydroxyl groups. The complex is a six-membered ring containing two oxygen atoms and one boron atom. The obtained sorption isotherms are processed using the Langmuir and Freundlich equations. This allowed assuming that the adsorption of borate ions on highly porous sorbents obeys the Langmuir model.

Шляхом проведення традиційного двостадійного процесу карбонізації–активації було одержано зразок нанопоруватого вугілля із лігноцелюлозної сировини — кісточок кизилу, а також його аналог, модифікований саліциловою кислотою. Визначено порометричні характеристики

одержаних зразків вугілля на основі ізотерм сорбції–десорбції азоту. Встановлено, що приготовлені вугілля мають розвинену порувату структуру з високою питомою поверхнею $S_{\text{ВЕТ}} = 1450 \text{ м}^2/\text{г}$, питомою поверхнею мезопор $S_{\text{me}} = 350 \text{ м}^2/\text{г}$, сумарним об'ємом пор $V_{\Sigma} = 0,7 \text{ см}^3/\text{г}$. Зроблено припущення щодо можливості використання таких сорбційних матеріалів для очищення водних джерел від йонів В(III). Для обох зразків було проведено сорбційні дослідження з поглинання Бору з водних розчинів. Вивчено сорбційну здатність активованого та додатково модифікованого саліциловою кислотою вугілля по відношенню до йонів Бору як мікродомішок, що містяться в природних водах. Показано, що максимальні сорбційні властивості має модифікований препарат, адсорбційна здатність якого досягає максимального 18 мг/г. Зроблено припущення про вірогідний механізм сорбції йонів Бору. Було показано, що в гетерогенних системах присутність кисневмісних функціональних груп дуже ефективна в процесах, пов'язаних з видаленням борних забруднювачів. Борат-йон атакує гідроксильні групи фенольного кільця й утворює координаційний зв'язок між атомом Бору у борат-йоні й атомом Оксигену у гідроксильних групах. Комплекс представляє собою шестичленне кільце, яке містить два атоми Оксигену та один Бору. Одержані ізотерми сорбції обробляли з використанням Ленгмюрового та Фройндліхового рівнянь. Це дало змогу стверджувати, що адсорбція борат-йонів на високопористих сорбентах підпорядковується Ленгмюровому моделю.

Key words: cornel seed, activated carbon, boron, specific surface area, salicylic acid, adsorption capacity.

Ключові слова: кизилова кісточка, активоване вугілля, Бор, питома поверхня, саліцилова кислота, сорбційна здатність.

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1. INTRODUCTION

In recent years, there has been a rapidly growing interest concerning the widespread environmental pollutions [1], which emerged as one of the urgently demanding priorities. It is needed to say that the impact of pollution threatens to environment and public health, causing the destroy of natural sources: water, air and soil as well as the growth of the pollution-initiated diseases hepatic failures, respiratory system disorders, heart diseases, allergy, skin diseases and many others.

Boron compounds are used in the manufacture of glass, soaps and detergents and as flame retardant. In general, living organism consumes the greatest amount of boron substances through food intake, as it is naturally found in many edible plants. Boron is also found in groundwater, but its presence in surface water is frequent-

ly a consequence of discharge between the treated sewage effluent, in which it arises after applying of some detergents, and surface waters. The consuming of small concentration of this element is safety but its higher content become dangerous for human health [2]. Toxicological studies have shown that short- and long-term oral taking of boric acid or borax by laboratory animals may affect the male reproductive ability.

The application of usual water treatment (coagulation, sedimentation, and filtration) does not essentially promote the boron removal, and the sorption methods need to be installed in order to remove boron from waters. Numerous works have been done for boron removal from aqueous solutions. Some of the processes that have been used were as follow: activated carbons [3], surface modified cellulose derivatives [4] and soils [5]. It was established that boron removal occurs due to adsorption on external surface as well as due to ion exchange [6].

Among others, lignocellulosic precursors present highly recommendable sources because they are readily available, low-cost, regularly produced and renewable feedstocks. Fruit stones and shells [7–9] are particularly interesting as they are generated as by-products from food processing industries in amounts sufficient for obtaining good adsorbents. This would contribute to solving many current-day environmental purification problems. Accordingly, investigation has been directed to the utilization and upgrading of biomass materials for the production of high porous carbons [10–14]. Cheaper activated carbons are not only abundant low-cost materials but, moreover, they are the products of relatively low-cost process of preparation.

Among a large variety of adsorbents, activated carbon of lignocellulosic origin is still the most important one in current use in the environmental pollution control due to its large surface areas, high adsorption capacity, porous structure, selective adsorption and high purity standards [15]. Nevertheless, there are a number of factors affecting the adsorption capacity of activated carbon and adsorption degree of some toxic trace elements. Therefore, the adsorption capacities and the feasible removal rates of the activated carbon must be substantially boosted for boron ions by the modification with suitable reagent. Over the recent several years, the development of surface modified activated carbons served as a springboard for improving the properties of existing activated carbons. Surface modified activated carbons proved to have superior adsorption capacity towards boron substances, which are less adsorbed by non-modified activated carbons [5, 16].

The aim of the present investigation was to obtain activated carbon from novel lignocellulosic precursor—cornel seed, impregnating with salicylic acid to prepare its modified derivative, to investigate

the textural properties of both carbons and to study removal capacity towards B(III) ions.

2. EXPERIMENTAL

Cornel seed obtained from Ukrainian cornelian cherry was used as a precursor in the present study. Two-step physical activation method was used to prepare the activated carbon. At first, carbonization was carried out to produce chars with rudimentary pore structure. The second stage comprised steam activation of chars at a temperature of 850°C to produce the final product with well-developed external porous structure.

The process of obtaining the surface modified carbon included the impregnation of activated carbon with solution of salicylic acid. After impregnation, soaked samples were dried at a temperature of 80°C for about 1 hour.

The data on the porous structure of the synthesized carbons were obtained from nitrogen sorption–desorption isotherms at a temperature of 77 K using a NOVA 2200 gas adsorption analyser (Quantachrome, USA). Before the measurements, the samples were kept in a vacuum of $1 \cdot 10^{-4}$ Torr at 180°C for 16–20 hours. The specific surface area was calculated by the BET method (S_{BET}). Pore size distribution (PSD) was obtained using the BJH method. The total pore volume was estimated from the volume of liquid nitrogen adsorbed at a relative pressure $p/p_0 = 0.99$.

To study removal capacity, 0.05 g of carbon was shaken with 25 ml of boric acid solution with following concentrations: 10, 20, 30, 40 and 50 mg/l for 6 hours in rotating shaker at room temperature. The B(III) ion content in aqueous phase was determined by means of spectrophotometric method. 10 ml of the tested solution was placed in a porcelain cup and 1 ml of a 10% NaCl solution and dropwise 10% NaOH solution were added until an alkaline reaction. The solution was evaporated to dryness in a water bath. To the cooled dry residue, 15 ml of a 0.005% solution of carmine in concentrated sulfuric acid were added from the burette. The solution was thoroughly mixed with a glass rod until the dry residue is completely dissolved and the evolution of hydrogen chloride stops. The solution was transferred into a colorimetric test tube with a ground stopper. On the next day, the solution was mixed again and placed in colorimetric device FEK-M (30 mm cuvette, wavelength of 620 nm). A 0.005% solution of carmine in sulfuric acid was used as a reference with zero B content.

The equilibrium concentrations were then defined using a previously established calibration graph. The adsorption capacity of boron removal from aqueous solution was determined from the formula:

$$A = (C_o - C_e) \frac{V}{m}, \quad (1)$$

where A is the amount of B(III) adsorbed at equilibrium, (mg/g), C_o is the initial concentration of B(III) (mg/l); C_e is the equilibrium concentration of B(III) (mg/l), V is the volume of solution, from which adsorption occurs (l); m is the adsorbent mass (g).

3. RESULTS AND DISCUSSION

B-ions adsorption was carried out on obtained activated carbon and activated carbon previously impregnated with salicylic acid. In present investigation, surface modification of obtained carbon was performed to prepare of oxygen functional group-supported adsorbent (OFG). The choice of this chemical reagent was caused due to presence of OFG groups.

Figure 1 shows the nitrogen adsorption-desorption isotherms of activated carbon prepared from dogwood stone and its surface modified derivative. It is seen that the adsorption-desorption isotherms for investigated carbons may be related to Type IV according to IUPAC classification [17]. Characteristic features of derived isotherm are its hysteresis loop, which is associated with capillary condensation taking place in mesopores, and the limiting uptake over a range of high p/p_o values. The initial part of IV isotherm is attributed to monolayer-multilayer adsorption since it follows the same path as the corresponding part of a Type II isotherm obtained with the given adsorptive on the same surface area of the adsorbent

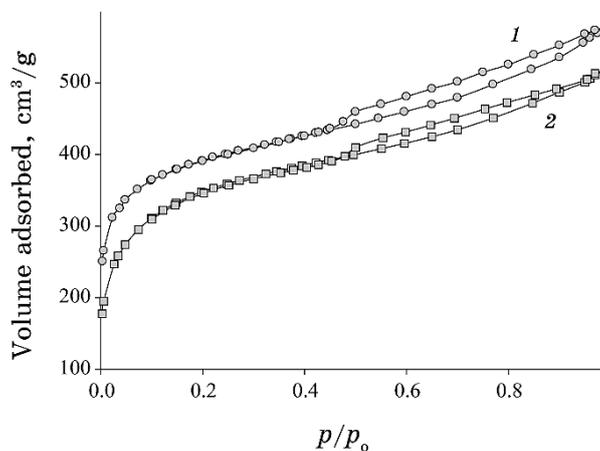


Fig. 1. Nitrogen adsorption-desorption isotherms of activated carbon (1), prepared from cornel stone, and its modified derivative (2).

in a non-porous form. These isotherms are characterized with wide hysteresis loop whose closure points are varied between $p/p_0 = 0.45$ and $p/p_0 = 0.95$. It testifies about significant lot of mesoporosity of carbons produced. The comparison of obtained activated carbon and its modified derivative shows that surface modification results to decreasing of volume adsorbed at a $p/p_0 \cong 0.98$ from $570 \text{ cm}^3/\text{g}$ to about $490 \text{ cm}^3/\text{g}$.

The pore size distributions of prepared carbons are presented in Fig. 2. It is seen that investigated carbons contain both micro- and mesopores. The plot features predict the prevalence of microporosity in tested carbons though the mesopore lot is significant. The pore size distribution is characterized by a large peak at effective pore radius equal 1.97 nm for activated carbon and 2.03 nm for modified carbon. It may be concluded that this little difference is caused by the surface modification procedure. The BET surface areas, external areas, micro and total pore volumes, calculated from adsorption–desorption isotherms as well as an average pore radius, are presented in Table 1. It can be seen from the table that, because of modification, the character-

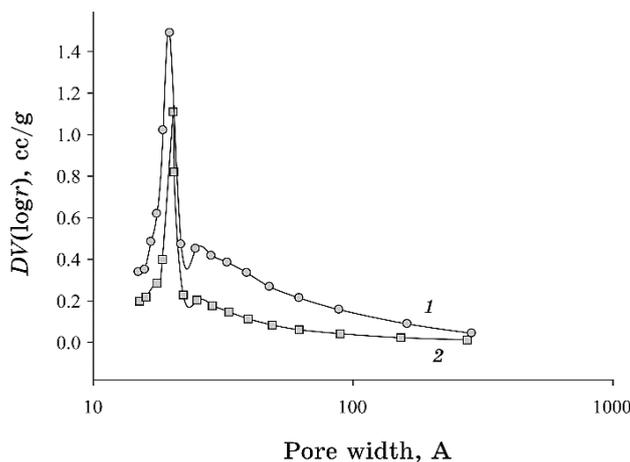


Fig. 2. Differential pore size distribution obtained from the desorption branch of the isotherm for activated carbon (1), prepared from cornel stone, and its modified derivative (2).

TABLE 1. Porometric characteristics of prepared carbon and its modified analogue.

Samples	A_{BET} , m^2/g	A_{EXT} , m^2/g	V_{mi} , cm^3/g	V_t , cm^3/g	R_{eff} , Å
Activated carbon	1450	351.2	0.46	0.70	19.70
Modified carbon	1345	325.8	0.42	0.66	20.30

istics of the porous structure slightly decrease in comparison with the characteristics of unmodified carbon, the specific surface of which is of 1450 m²/g, the surface of mesopores is of 350 m²/g, and the total pore volume reaches 0.7 cm³/g.

It is known that the adsorption capacity depends on some factors. First of all, it is influenced by the activated carbons' texture characteristics as well as surface chemistry (surface functional groups). The complexation reaction between borate ions and oxygen-containing groups of salicylic acid was studied in an aqueous solution. The results show that complexation can proceed completely and rapidly at room temperature. It was shown that adsorption capacity (Fig. 3) is strongly increased with applying of surface modification and obtaining OFG-supported activated carbon reaching about 18 mg/g of sorbent. It was established that, in spite of higher external surface area of activated carbon, the sorption capacity of its modified derivative is increased almost 2 times towards boron-containing pollutant (Fig. 3). In heterogeneous systems, the presence of OFG groups has been demonstrated to be very effective in processes, connected with removal of boron ions [18]. The borate ion attacks the hydroxyl groups of the phenolic ring and forms a coordination bond between the boron atom in the borate ion and the oxygen atom in the hydroxyl groups. The complex is a six-membered ring containing two oxygen atoms and one boron. Complexation can release hydrogen ions, which leads to a decrease in the pH of the solution.

Results obtained are in a good agreement with works devoted to surface modification of an inorganic support material, MCM-4.1, with N-methylglucamine for boron uptake from aqueous solutions [19]. According to this work, the maximum amount of B (as H₃BO₃) that may be adsorbed by such modified material was found to be 0.8 mmol/g of sorbent.

To determine the adsorption model of boric acid on the obtained sorption materials, the experimental results were processed using the Langmuir and Freundlich equations:

$$A = A_{\infty} \frac{KC_{eq}}{1 + KC_{eq}}, \quad (2)$$

where A_{∞} is a value of boundary adsorption (mg/g), K is the constant of the Langmuir equation; C_{eq} —equilibrium concentration of adsorbate (mg/dm³);

$$A_F = K_F C^{1/n}, \quad (3),$$

where A is the amount of adsorption (mg/g), n is an exponent.

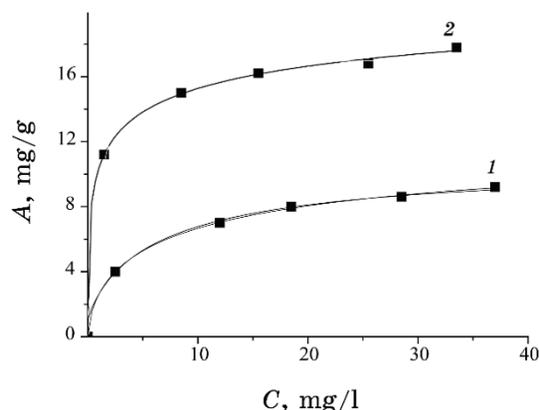


Fig. 3. Isotherms of adsorption of B(III) ions on activated carbon from cornel seed (1) and its analogue modified with salicylic acid (2).

TABLE 2. Parameters of the Langmuir and Freundlich isotherms for nanoporous carbon and its modified analogue.

Samples	Langmuir isotherm			Freundlich isotherm		
	A_{∞} , МГ/Г	K	r^2	K_F , МГ/Г	n	r^2
Active carbon	12.9	9.05	0.997	10.8	0.87	0.953
Modified active carbon	24.7	2.51	0.989	17.2	1.31	0.956

The parameters of the Langmuir equation (A_{∞} , K) and the Freundlich one (A_F , n), as well as the correlation coefficients (r^2) of these dependences, were calculated using the least squares method and are given in Table 2. High values of the correlation coefficients indicate that the adsorption of boric acid on highly porous sorbents obeys the Langmuir model.

4. CONCLUSIONS

By means of the traditional two-stage carbonization–activation process, a sample of activated carbon was obtained from a cornel seed. From the standpoint of industrial applications, carbon is suitable adsorbent with high surface area ($S_{BET} = 1450 \text{ m}^2/\text{g}$, $S_{me} = 350 \text{ m}^2/\text{g}$, $V_{\Sigma} = 0.7 \text{ cm}^3/\text{g}$).

It was found that adsorption of boron onto carbonaceous surface was enhanced by its modification with salicylic acid and obtaining of OFG-supported derivative. It was shown that modified carbon exhibits the maximum sorption properties, the adsorption capacity of which reaches 18 mg/g. An assumption has been made about the

mechanism of boron ions adsorption. In heterogeneous systems, the borate ion attacks the hydroxyl groups of the phenolic ring and forms a co-ordination bond between the boron atom in the borate ion and the oxygen atom in the hydroxyl groups. In result, it was determined that the use of salicylic acid as an impregnant for activated carbon led to the increase of the amount of boron adsorbed.

The processing of experimental data using the Langmuir and Freundlich equations suggests that the adsorption of borate ions on highly porous adsorbents obeys the Langmuir model. By means of the traditional two-stage carbonization–activation process, a sample of activated carbon was obtained from a cornel seed. From the standpoint of industrial applications, carbon is suitable adsorbent with high surface area ($S_{BET} = 1450 \text{ m}^2/\text{g}$, $S_{me} = 350 \text{ m}^2/\text{g}$, $V_{\Sigma} = 0.7 \text{ cm}^3/\text{g}$).

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