

EVALUATING AND IMPROVING THE EFFICIENCY OF THE USE OF ACTIVATED CARBONS FOR THE EXTRACTION OF ORGANOCHLORINE COMPOUNDS IN WATER TREATMENT TECHNOLOGY

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Abstract: Removing small amounts of organochlorine compounds from aqueous solutions is important for the water treatment and wastewater treatment. Sorption methods with the use of carbon sorbents proved to be very successful in some cases. The paper studies the adsorption equilibrium in the systems carbon sorbent (active carbons KAU, AG-OV-1, SKD-515, semi-coke) – aqueous solutions of chloroform, chlorophenol and carbon sorbent – aqueous solutions of mixtures of these organochlorines. The research holds that the known adsorption equations can be used to describe the adsorption equilibrium and to calculate the main parameters of sorption. The paper discusses the possible mechanisms of chloroform and chlorophenol sorption by active carbons from aqueous solutions. It identifies those brands of activated carbons, which most effectively extract chloroform and chlorophenol from the treated water. The authors examine the possibility of the reagent modification of the sorbents by acid and alkali solutions in order to increase the adsorption capacity.

Keywords: active carbon, chloroform, chlorophenol, adsorption, equilibrium, modification

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INTRODUCTION

Currently, the level of pollution is so high, that the ecosystem and people's health are endangered. This also applies to the natural water that is used for industrial and household needs. Over the last 10 years, the number of sub-standard samples for chemicals in the natural water sources, used for the centralized water supply in the Kemerovo region, has increased, and this indicates that the quality of the natural water has deteriorated. According to the data of the Kemerovo Centre of hydrometeorology and monitoring of environment (Kemerovo, Russia) – the branch of Western-Siberian Department of State Meteorological Service (Novosibirsk, Russia), the hazardous substances, including organochlorine compounds and a number of other substances, are found in the river Tom' and in the drinking water [1]. Summation indices show that such substances in the river water are up to 5 times greater than permissible levels; and up to 1.3 times higher in the drinking water [1]. In the preparation of drinking water, there occurs the partial transformation of its organic impurities and the formation of even more hazardous compounds than those that were originally present. This is why in Kemerovo, highly toxic organochlorine compounds in

concentrations that exceed the permissible levels from 1.3 to 10 times (based on summation of the action) were found in the drinking water that was sterilized by active chlorine [2].

Adsorbents of different nature, including carbon material, are used to extract small amounts of substances from the aqueous media. In some cases their use in water purification was very successful. This paper studies the possibility and effectiveness of the use of activated carbons that are derived from different raw materials, and that have different physical and chemical properties, and surface structure, to extract organochlorine compounds (chloroform and chlorophenol). Chloroform and chlorophenol are the main water pollutants that are being formed when water is disinfected with the use of chlorine or chlorine-containing disinfectants.

OBJECTS AND METHODS OF STUDY

The paper examines the systems which include active carbons of KAU, AG-3, AG-OV-1, SKD-515, semi-coke (SC), as well as model aqueous solutions with varying content of chloroform (trichloromethane), chlorophenol (4-chloro-1-oksibenzol) and their mixtures [3]. The pre-treatment of active carbons and

semi-coke was carried out according to the method described in [4]. The sorbents were placed in distilled water for one day, then rinsed with fresh water to get rid of dust fractions, then they were dried to achieve the air-dry state, and then they were heated at $105.0 \pm 0.10^\circ\text{C}$ for 3 hours (to remove the "external" moisture [5]). Dried samples were cooled in a desiccator and stored in a hermetically sealed container.

The detection of chloroform in the aqueous solution was done by the method of gas chromatography as described in [6], and the detection of chlorophenol was done by the method described in [7].

The adsorption equilibrium in the system *aqueous solution – active carbon* was studied under static conditions by placing a constant accurate sample of sorbent in the aqueous solutions of chloroform, chlorophenol or their mixtures, with a given concentration; then the system was shaken for sufficient time to achieve the adsorption equilibrium [8]. The adsorption equilibrium time in the system *sorbent – solution* was determined in a previous series of experiments, and it did not exceed 20 hours. Thus, the duration of the contact between the *sorbent* and the *solution* was 24 hours for all samples.

Then the weighed amount was filtered off with a paper filter, and the concentration of the organic component was detected in the filtrate.

The amount of the equilibrium adsorption (a , mmole/g) was calculated using the formula:

$$a = \frac{(C_0 - C_p)V}{m}, \quad (1)$$

where C_0 and C_p are the initial and the equilibrium concentration of the substance in solution, accordingly, mmole/dm³; V is the volume of the solution from which the adsorption is performed, dm³; m is the mass of the sorbent sample, g.

The adsorption isotherms were determined based on the experimental data. We used the Freundlich equation to describe the adsorption equilibrium of the studied systems [9]:

$$a = \beta C_p^{1/n}, \quad (1)$$

where β represents the value of the adsorption under the equilibrium concentration of the adsorptive, which equals 1 mole/dm³; $1/n$ characterizes the degree of approximation to the isothermal line.

Langmuir equation [9]:

$$a = \frac{a_{\max} K \cdot C_p}{1 + K \cdot C_p}, \quad (2)$$

where a is the value of the adsorption at equilibrium concentration of C_p ; a_{\max} is the value of the limiting adsorption; K is the adsorption equilibrium constant.

BET equation [9]:

$$a = a_m \frac{K}{\left(1 - \frac{C_p}{C_s}\right) \left[1 + (K-1) \frac{C_p}{C_s}\right]} \cdot \frac{C_p}{C_s}, \quad (3)$$

where a_m is the adsorptive capacity of the saturated monolayer, which is determined by the size of the "landing" area of the solute molecule, mmole/g; K is

the constant of the equation of the multilayer adsorption; C_p and C_s represent the concentration of the equilibrium and saturated solutions, respectively, mmole/dm³, and the equation of Dubinin-Radushkevich to calculate the adsorption of substances from aqueous solutions [10]:

$$\lg a = \lg a_\infty - 2.303 \frac{R^2 T^2}{\beta^2 E^2} \left(\lg \frac{C_s}{C_p} \right)^2, \quad (1)$$

where T is temperature, K; β is the coefficient of similarity; E is the characteristic energy, kJ/mole; C_s and C_p represent the concentration of the equilibrium and saturated solutions, mmole/dm³.

RESULTS AND DISCUSSION

We studied the equilibrium adsorption of chloroform and chlorophenol from unicomponent (for organic substance) aqueous solutions. The adsorbents were active carbons and semi-coke. We used a broad range of the concentrations of the extracted components. The purpose was:

- to determine if the known absorption equations can be applied to describe the sorption behaviour of the studied systems;
- to calculate the basic sorption parameters;
- to study establishing adsorption mechanisms;
- as well as to measure the changes in the absorption mechanisms as the concentration increases during the transition from a low concentration to the limiting solubility of the components in water.

Experimental isotherms of the chloroform adsorption are shown in Fig. 1.

Based on their shape, the isotherms of the chloroform adsorption can be referred to the isotherms of L-type under the classification [11]. This allows us to suggest the physical nature of the interaction *sorbent – sorptive*.

We found that the above equations satisfactorily describe the adsorption isotherm of chloroform. Hence, these equations can be applied for the calculation of the basic adsorption parameters needed to create the sorption technology of the extraction of contaminants from water. The adsorption isotherms have a classic form, and the maximum adsorption capacity increases in the following sequence:

$$\text{SC} < \text{AG-OV-1} < \text{AG-3} < \text{SKD-515} < \text{KAU}.$$

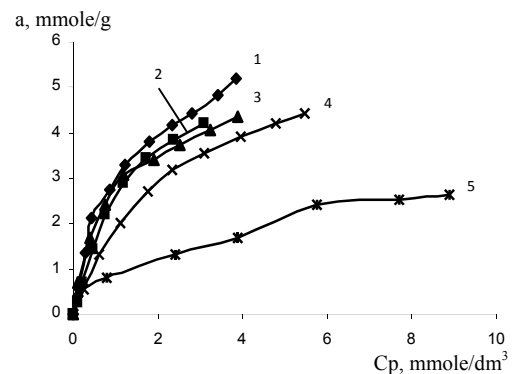


Fig. 1. The isotherms of the adsorption of chloroform from aqueous solutions: 1 – KAU; 2 – SKD-515; 3 – AG-3; 4 – AG-OV-1; 5 – SC.

The data presented in Fig. 1 show that the preference in the choice of the brand of the activated carbon used to extract the chloroform should be given to the KAU. However, given the cost of raw materials for the production of this type of coal (the shell of pits from fruit trees) and the lack of the industrial capacity for its production, the recommended brands of active

carbons to extract chloroform must be SKD-515 and AG-3, which have similar sorption characteristics with respect to chloroform.

We calculated the basic parameters for the adsorption of sorbents, that are supposedly effective for the chloroform extract from aqueous solutions (Table 1).

Table 1. The parameters of chloroform adsorption

| sorbent Brand | Types of equations | | | | | | | | | |
|---------------|----------------------|------------|-------------------------------|------------|-----|----------------------|------|------------|----------------------|-----|
| | Dubinin-Radushkevich | | | Freundlich | | BET | | | Langmuir | |
| | a_{\max} , mmole/g | E, kJ/mole | W , dm^3/kg | β | 1/n | a_{\max} , mmole/g | K | Q, kJ/mole | a_{\max} , mmole/g | K |
| SKD-515 | 8.0 | 8.5 | 0.9 | 2.3 | 0.7 | 5.5 | 33.5 | 8.8 | 6.3 | 0.7 |
| AG-3 | 5.9 | 10.5 | 0.6 | 2.6 | 0.4 | 4.6 | 58.7 | 10.1 | 5.3 | 1.1 |
| SC | 3.5 | 7.0 | 0.4 | 1.5 | 0.7 | 3.2 | 9.9 | 5.9 | 5.0 | 0.1 |

Due to the fact that chlorophenol often accompanies chloroform in purified water, and, as a rule, the concentration of chloroform is higher than chlorophenol, to extract both components from the purified water and to study the equilibrium sorption chlorophenol, we selected active carbons SKD-515 and AG-3. The interaction between the semi-coke SP and chlorobenzene were of particular practical interest. It is not only because it is significantly less expensive and is manufactured in Kuzbass, but because after the adsorption, it can be used as fuel. Fig. 2 shows the experimental adsorption isotherms of chlorophenol from aqueous solutions by the activated carbons SKD-515, AG-3 and SC.

The sorption behaviour of chlorophenol with these brands of adsorbents is similar to the behaviour of chloroform. The earlier mentioned adsorption equations can be used to describe isotherms of adsorption and for calculating the basic parameters of

adsorption. The chlorophenol sorption parameters are shown in Table 2.

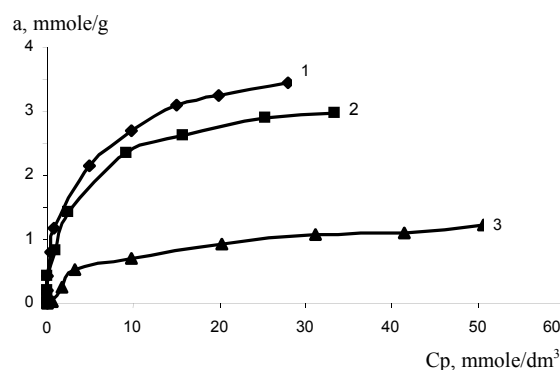


Fig. 2. The isotherms of the adsorption of chlorophenol from aqueous solutions: 1 – AG-3; 2 – SKD-515; 3 – SC.

Table 2. The parameters of the chlorophenol adsorption

| sorbent Brand | Types of equations | | | | | | | | | |
|---------------|----------------------|------------|-------------------------------|------------|-----|----------------------|------|------------|----------------------|-----|
| | Dubinin-Radushkevich | | | Freundlich | | BET | | | Langmuir | |
| | a_{\max} , mmole/g | E, kJ/mole | W , dm^3/kg | β | 1/n | a_{\max} , mmole/g | K | Q, kJ/mole | a_{\max} , mmole/g | K |
| SKD-515 | 2.9 | 14.1 | 0.3 | 1.0 | 0.3 | 2.7 | 138 | 12.2 | 3.1 | 0.4 |
| AG-3 | 3.6 | 13.5 | 0.4 | 1.1 | 0.4 | 3.0 | 186 | 13.0 | 3.5 | 0.6 |
| SC | 1.7 | 8.0 | 0.2 | 0.1 | 0.7 | 1.0 | 66.9 | 10.4 | 1.4 | 0.1 |

The analysis of the values of the adsorption volume W , presented in Tables 1 and 2, which are in the range of 0.2–0.4 dm^3/kg for the chlorophenol adsorption and 0.4–0.9 dm^3/kg for the chloroform adsorption, leads to the conclusion that the adsorption of chlorophenol and chloroform from individual aqueous solutions is subject to micropore volume filling mechanism. The characteristic energy values E of the chloroform adsorption (Table 1) and chlorobenzene (Table 2) indicate that the adsorption takes place mainly in the micro- and meso-pore adsorbents [12].

The heat of the adsorption of chloroform by the tested sorbents' brands does not exceed 10.13 k/mole (Table 1), which indicates that the adsorption of

chloroform is caused by the van der Waals forces (non-specific interaction). The heat of the chlorophenol adsorption by the tested sorbents is significantly higher than of the chloroform adsorption (Table 2). This indicates that in addition to the dispersion of nonspecific interactions, we observe a specific physical adsorption. This is due to the fact that the oxygen-containing surface functional groups of activated carbon can form hydrogen bonds with the substituents of the aromatic ring of chlorophenol. In addition, the aromatic ring of chlorophenol is an acceptor of the electron density. This allows us to assume the formation of donor-acceptor complexes of the type *dipole – dipole* attraction, as the donor is able to

provide an electron pair to bond formation; whereas the acceptor (chlorophenol) does not have a vacant orbital. During the chlorophenol adsorption, the oxygen of surface carbonyl groups plays role of an electron donor, whereas the π -electron system of the aromatic ring plays role of an acceptor [13].

Thus, the study of the equilibrium of the adsorption of chlorophenol and chloroform from individual aqueous solutions by the tested brands of carbons allowed us to calculate the basic adsorption characteristics and to determine that the carbon brands SKD-515, AG-3 are the most effective abstractors of organochlorines from aqueous solutions. In the case of chloroform, semi-coke SC has a low adsorption capacity, compared with SKD-515 и AG-3. In this regard, we did not proceed with the further research of the sorption behaviour of the semi-coke.

We studied the equilibrium sorption of a mixture of chloroform and chlorophenol from an aqueous solution with the range of concentrations used in the actual practice of water treatments with chloramines for disinfection (Fig. 3 and 4). We tested the adsorption of chlorophenol and chloroform from their mixtures in the components' ratio 200 : 1 (mmole/dm³) using SKD-515 and AG-3. Having compared the adsorption isotherms of chlorophenol and chloroform from their aqueous mixtures with the adsorption isotherms of the aqueous solutions of the individual components (Fig. 3

and 4), we found that the absorption is weaker when the two components are combined. In this case, the adsorption of chloroform is higher than the chlorophenol adsorption, probably due to its lower solubility in water ($C_{\text{chlorophenol}} = 210.8 \text{ mmole/dm}^3$, $C_{\text{chloroform}} = 68.67 \text{ mmole/dm}^3$). It is also lower due to its smaller (compared to chlorophenol) van der Waals' molecule size (0.64 nm chloroform; 0.8 nm chlorophenol).

When extracting organic compounds from their aqueous mixtures we observed the change of the isotherm shape for chlorophenol (Fig. 4, curves 3 and 4) from L to S₄ [9]. That may indicate a change in the nature of the components' interactions in the solution and with the surface of the AC. Changing forms of adsorption indicates a fierce competition between the molecules of chlorophenol, chloroform and water for room in the AC's pores.

We found that the Freundlich and BET's equations don't work for the description of the adsorption equilibrium in the system *water – chlorophenol – chloroform – AC* due to the large deviation of the calculated adsorption isotherms from the experimental ones. The adsorption isotherms based on the equations Dubinin-Radushkevich and Langmuir coincide with the experimentally obtained isotherms. Table 3 represents the equilibrium sorption parameters calculated using this equation.

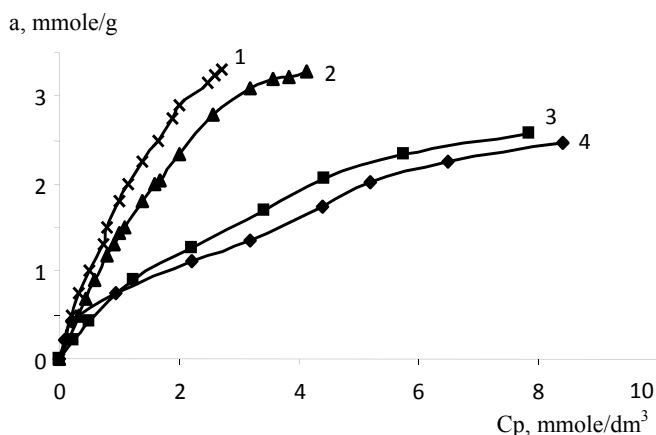


Fig. 3. The adsorption isotherms of chloroform from an aqueous solution: 1 – SKD-515; 2 – AG-3; 3 – SKD-515 (in the presence of chlorophenol); 4 – AG-3 (in the presence of chlorophenol).

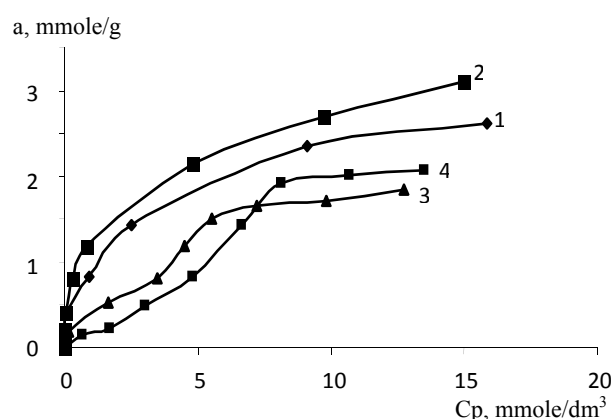


Fig. 4. The adsorption isotherms of chlorophenol from aqueous solutions: 1 – SKD-515; 2 – AG-3; 3 – SKD-515 (in the presence of chloroform); 4 – AG-3 (in the presence of chloroform).

Table 3. The parameters of chlorophenol and chloroform adsorption from aqueous solutions

| Sorbent Brand | Type of equations | | | | | | | | | |
|---------------|---|------------|---------------------------|----------------------------|-----|---|------------|---------------------------|----------------------------|-----|
| | chlorophenol adsorption in the presence of chloroform | | | | | chlorophenol adsorption in the presence of chloroform | | | | |
| | Dubinin-Radushkevich | | | Langmuir | | Dubinin-Radushkevich | | | Langmuir | |
| | a_{max} , mmole/g | E, kJ/mole | W , dm ³ /kg | a_{max} , mmole/g | K | a_{max} , mmole/g | E, kJ/mole | W , dm ³ /kg | a_{max} , mmole/g | K |
| SKD-515 | 8.0 | 8.5 | 0.9 | 6.3 | 0.7 | 2.9 | 14.1 | 0.3 | 3.1 | 0.4 |
| AG-3 | 5.9 | 10.5 | 0.6 | 5.3 | 1.1 | 3.6 | 13.5 | 0.4 | 3.5 | 0.6 |

The limit value for the adsorption volume W of active carbon SKD-515 and AG-3 vary from 0.3 to 0.4 dm³/kg (for chlorophenol) and from 0.6 to

0.9 dm³/kg (for chloroform). This allows us to suggest that the adsorption of chlorophenol and chloroform, when they are both present in the solution, is subject to

the volumetric filling of the micropores. The characteristic energy values indicate that the chloroform and chlorophenol sorption at their simultaneous presence in the solution occurs mainly in the meso- and micropores. The values of the heat adsorption indicate a non-specific dispersion interaction of chloroform with the sorbent. As for chlorophenol, the values of the heat adsorption also indicate a certain contribution to the specific physical adsorption on active centers. The type of AC defines the distribution of macro-, micro- and mesopores, which, in its turn, determines their availability for the molecules of sorbed substances [13]. For chloroform, sorbed due to the non-specific interaction, the only option is the adsorption in the pores. For chlorophenol, the adsorption on oxygen-containing groups is possible, as evidenced by the data in Fig. 2 and Fig. 4, from which it follows that the chlorophenol sorbed by AC AG-3 is better than by AC SKD-515. We found that the surface of AC-3 is more oxidized and it contains a variety of oxygen-containing groups, which significantly contributes to the overall amount of adsorption.

Thus, based on the equilibrium sorption studies, we established the main parameters of the chloroform and chlorophenol adsorption by active carbons from the individual aqueous solutions and aqueous mixtures of these components. We analyzed the adsorption mechanisms which determine the adsorption capacity and efficiency of extraction. This allows us to identify the brands of activated carbons which possess the optimum extraction properties.

The modification of the sorbents

The major principle of the development of the adsorption technology is to increase the adsorption capacity of sorbents. This can be achieved by changing the structure and surface of the adsorbent through the use of various types of modifiers. The modification of carbon materials is widely used to increase their lyophilic and adhesive properties, as well as their reaction and ion-exchange capacity. The solutions of mineral acids, bases, organic reagents, as well as various types of oxidizing agents are used as modifiers. We studied the liquid phase reagent modification.

In [14] it is noted that the presence of iron salts in the active carbon catalytically decomposes some organic adsorbing substances, so it should be removed from the surface of active carbon during the adsorption studies.

To find out that during the AC treatment with diluted hydrochloric acid and sodium hydroxide solutions, with a concentration of 1.5–2.0 mole/dm³, the iron ions (III) are intensely washed off. This is evidenced by the ash content of the respective carbons, which is reduced on average by 18% [2].

We found that the treatment of active carbons with solutions of hydrochloric acid and sodium hydroxide reduces the adsorption capacity of chloroform, as evidenced by the data in Fig. 5.

The decrease in the adsorption of chloroform in the carbons treated by reagents, may be associated with the transition of part of the micropores into mesopores. We found that the reagent processing changes the state of the surface of the adsorbent, which may occur due to the formation of additional oxygen-containing functional groups of the acid type, which is evidenced by the potentiometric titration by Bem [15] (Fig. 6).

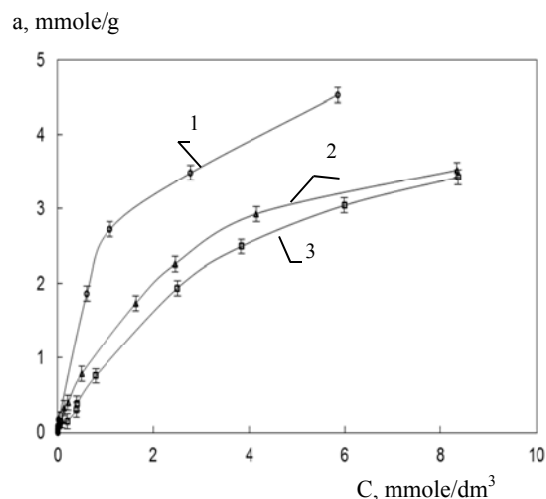


Fig. 5. The adsorption isotherms of chloroform on the SKD-515: 1 – Original; 2 – processed by HCl; 3 – treated by NaOH.

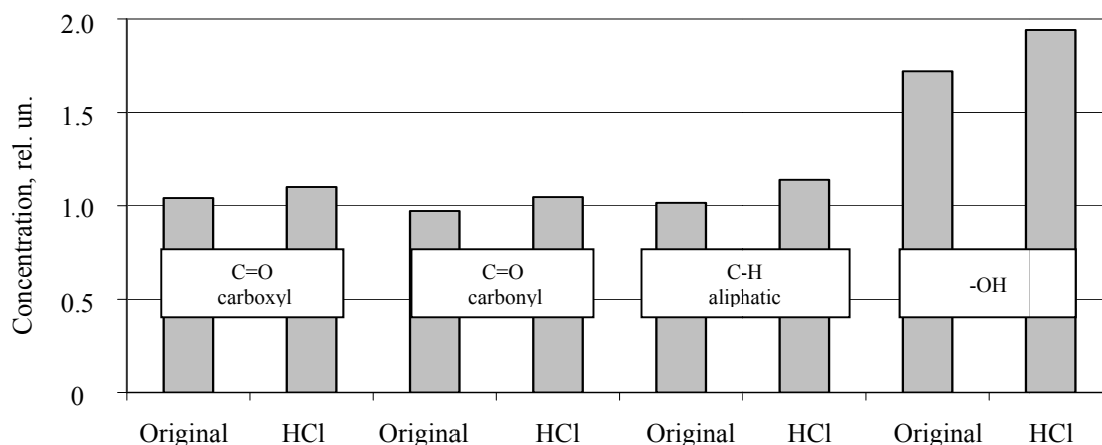


Fig. 6. The effect of reagent treatment on the surface condition of AC SKD-515.

The AC reagent treatment with hydrochloric acid or sodium hydroxide leads to an increase in the sorption capacity with respect to chlorophenol, which is connected, as shown above, with the ability of chlorophenol to the specific interaction with the surface formed after the treatment with oxygen-containing functional groups. In this regard, we should be

selective in the treatment (modification) of AC, used for the extraction of chloroform and chlorophenol from aqueous solutions. We should take into consideration the concentration ratio of the components in the solution, since an increase in the sorption capacity for one component of the test mixture is accompanied by a decrease in another.

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