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Sorption of Lead (II) ions from Aqueous Solutions by Carbon and Clay Sorbents.

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ABSTRACT

The work presents the results of research of montmorillonite-containing clay from several deposits and mineral occurrences of the Belgorod region, and the use of char and activated coal as sorbents for water purification from ions of lead (II). Charcoal was prepared by heating of birch sawdust without access of air at a temperature of 400-450 °C. The kinetics of the sorption process was studied, sorption capacity of sorbents was determined that amounted to 0.071 - 0.081 mg/g. It was found that efficiency of purification of aqueous solutions containing 5 mg / l of lead ions (II) using clays from different deposits and mineral occurrences amounts 85.2 - 90.8 % wt, charcoal - 88.4 % wt, activated carbon - 97.6 wt %. The results obtained on the basis of chemical and mineral composition and colloidal-chemical properties of the studied sorbents have been explained.

Keywords: aqueous solutions, lead ions, sorption, montmorillonite clay, charcoal and activated carbon.

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INTRODUCTION

Lead is one of the heavy metals which is very widespread in the environment and hazardous to living organisms. In this regard, the issues of increasing the efficiency of water purification techniques with the use of the low-cost materials available are topical.

Now mechanical, chemical, physical and chemical, and biological methods of water purification are used. One of the physical and chemical methods of water purification is the sorption which may have the character of physical sorption, chemical sorption, and ion exchange between the sorbate and the sorbent.

In recent years, for water purification from heavy metal compounds mineral aluminosilicate sorbents are increasingly used, in particular: various clays, zeolites, zeolite-containing rocks, gaizes, etc. which have high absorbency. The sorption properties of clay rocks are largely determined by their chemical and mineralogical composition, the dispersive capacity of minerals (particle size), and the sign and the value of electrokinetic potential of the surface.

This work is a continuation of previous researches of Belgorod clays conducted by us to solve environmental problems [1-6].

The purpose of this work is a generalization and systematization of the research results for Belgorod clays of several deposits and mineral occurrences on their ability to absorb lead (II) ions from aqueous solutions.

At the same time the following specific tasks were set:

- Explain different sorption capacity of clays under study in terms of their chemical and mineralogical composition and some colloidal-chemical properties.
- Conduct a comparative analysis of the sorption capacity of clays and traditional widely used sorbents, charcoal and active carbon, and identify the most environmentally and economically efficient sorbent for water purification from ions of lead (II).

METHODS

We used in the capacity of lead (II) ions sorbents the following materials:

- Natural montmorillonite-containing clays from deposits Poljana and Sergijevka, and mineral occurences of Kupino in Belgorod region;
- Charcoal and activated carbon.

Bentonite-like clays occurring in the territory of the Belgorod region are associated with the deposits of Kiev Formation which is composed of clays, marls and clayey silts. Clay minerals of the montmorillonite group are layered aluminosilicates of structure type 2:1 with swelling crystal lattice and elementary blocks thickness 0.94 - 1.45 nm.

In this work we have used the charcoal produced from birch sawdust [2], and activated carbon (Tabulettae Carbonis activati) tablets of Russian production (synonym - Carbolene) in the capacity of carbon sorbents.

When setting up the experiment to study the sorption capacity it was important to identify dependencies linking the main parameters of the process: the concentration of sorbate, sorbent dose, i.e., sorbate/sorbent ratio, and the duration of their contact. Comprehensive analysis of the sorbents to determine their practical suitability for water treatment included determination of the kinetics of the process and sorption capacity.

Sorption of lead ions (II) was carried out under static conditions at a constant temperature (20° C) from the simulated solution of lead (II) nitrate with Pb^{2+} ion concentration of 5 mg / l. The sorbent was taken in an amount of 3 g per 50 ml. The weight ratio of the sorbate Pb (II) to the sorbent was 0.000083:1. The sorption was carried out for 15, 30, 45, 60, 75, and 90 minutes.

Determination of the concentration of lead ions in the filtrates was carried out with use of photometric method according to the standard procedure [GOST 18293-72] using the spectrophotometer SPECORD 50.

The content of montmorillonite were determined by adsorptive luminescent analysis based on cation sorption by clay of organic dyes - luminophors to form a coagulate of an organic-clay complex.

The mineralogical composition of the clay was determined by X-ray phase analysis (XPA). The phase composition of the samples were identified by a set of diffraction peaks characteristic for a particular structure.

The chemical composition of a natural clay was determined in two ways: by standard methods of classical analytical chemistry traditionally used in the geochemistry upon analysis of minerals and rocks, as well as by electron microprobe analysis with the energy dispersive analyzer EDAX combined with a scanning ion-electron microscope Quanta 200-3D.

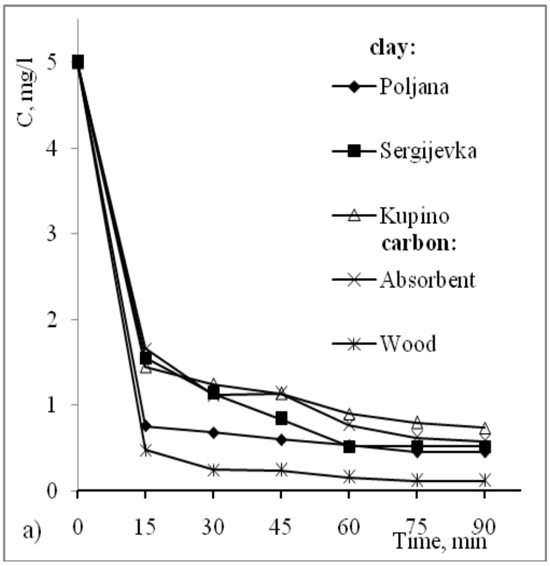
The particle sizes of the minerals composing the studied clays were determined using the above-mentioned microscope.

The zeta potential of the clay particles was measured using the analyzer Malvern Zetasizer Nano ZS.

MAIN PART

Results of the study of sorption capacity for clay samples with respect to the ions Pb (II) are shown in Figure 1.

The analysis of the kinetic curves (Fig. 1a) allows us to note that the major absorption of lead ions (II) by all sorbents is observed in the first 15 minutes. However, the sorption equilibrium is established after different time intervals: after 60 minutes in the case of use Sergijevka clay in the capacity of a sorbent, after 75 minutes for Poljana clay and activated carbon, and 90 minutes for Kupino clay and charcoal. The concentration of lead ions in solution with Poljana clay decreases in 10.9 times [7], with Sergijevka clay in 9.6 times [8], and with Kupino clay in 6.8 times [9]. Charcoal reduces the concentration of lead ions in solution in 8.6 times, and activated carbon reduces the concentration in 41.7 times [2]. Most smooth run of the kinetic curve is noted for Sergijevka clay.



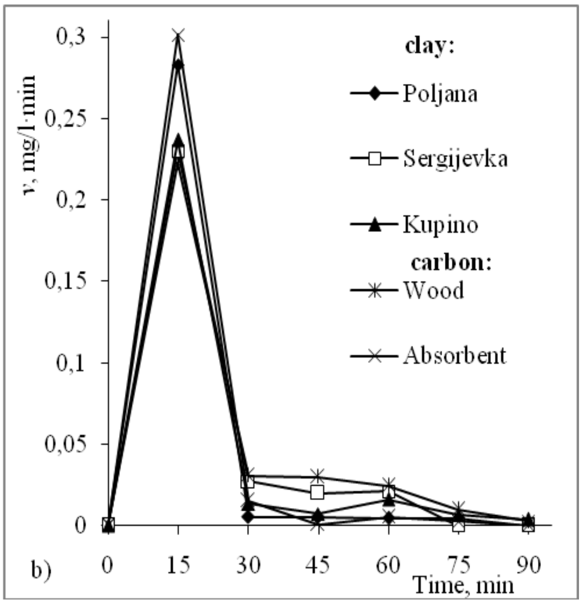


Fig. 1. Kinetics of Pb (II) ions sorption in aqueous solutions as a result of sorption by clays and coal: a) kinetic curves for reduction of Pb (II) ion concentration;
b) sorption rate change depending on the duration of the process

It follows from the profiles of changing the rate with time (Fig. 1b) that the maximum sorption rate for all clay sorbents has been noted in the first 15 minutes due to the attraction of lead (II) cations from the solution to the negatively charged surface of clay minerals. A large sorption rate is observed for the clay from the deposit "Poljana" (0.283 mg / l · min). Sergijevka and Kupino clays differ little by sorption rate from each other in the specified time interval. Sorption rates of these sorbents are equal to 0.230 mg / l · min, and 0.240 mg / l · min, respectively. The average rate of lead (II) ions sorption for the entire period of exposure (before the sorption equilibrium) for Poljana clay was 0.060 mg / l · min, Sergijevka clay - 0.075 mg / l · min, and Kupino clay - 0.047 mg / l · min.

The rate of lead ion sorption (II) by charcoal was less than by clay sorbents, and at an initial stage (first 15 minutes) is equal to 0.220 mg / l · min. Absorption of lead ions (II) under the same conditions with active carbon takes place at a higher rate (0.300 mg / l · min) due to the higher developed total surface of its pores as compared with charcoal.

The sorption capacity of the sorbents under study calculated on the basis of these data on the kinetics of the process was, respectively (mg / g): Poljana clay - 0.076; Sergijevka clay - 0.075; Kupino clay - 0.071; charcoal - 0.074; activated carbon - 0.081.

Purification efficiency of simulated aqueous solutions for lead ions (II) at a concentration of 5 mg / l (wt.%) makes: 90.8 with Poljana clay; 89.6 with Sergijevka clay; 85.2 with Kupino clay; 88.4 with charcoal; and 97.6 with active carbon.

Different capacity of clays under study to adsorb lead (II) ions is explained by differences in their material (mineralogical and chemical) composition, the content of the sorption-active minerals, different values of the absolute value of their electrokinetic potential, and particle size.

The mineralogical composition of clays of different deposits was defined on the basis of X-ray phase analysis (fig. 2).

The analysis of X-ray powder diffractograms has revealed that Poljana clay contains calcium and sodium montmorillonite (15.450, 12.923, 4.484, 2.592, 2.489, 1.767, 1.502 Å), illite (10.091, 4.484, 3.795, 3.236, 2.971, 1.639, 1.502 Å), kaolinite (7.161, 4.484, 2.592, 1.502 Å), clinoptilolite (8.131, 5.252, 3.976, 2.971, 2.800, 1.767 Å), calcite (2.489, 2.145, 2.018, 1.878 Å), pyrophyllite (2.407, 2.067, 1.767, 1.559 Å) hydromica (4.566, 3.607, 2.592, 1.767, 1.559Å), and feldspars (3.236, 2.330, 1.731, 1.595 Å).

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The composition of Sergijevka clay includes montmorillonite (11.556, 9.936, 2.603, 2.398 , 2.677 Å), kaolinite (7.284, 8.425 Å), low temperature trigonal quartz (4.529, 3.357 Å), magnetite (2.151, 1.969, 1.677, 4.529, 3.357 Å) , illite (6.487; 5.324 Å), and feldspars (3.261, 2.398, 1.735, 1.512 Å). Accessory minerals are dolomite, galuazit, palygorskite, pyrrhotite, muscovite, hydromica.

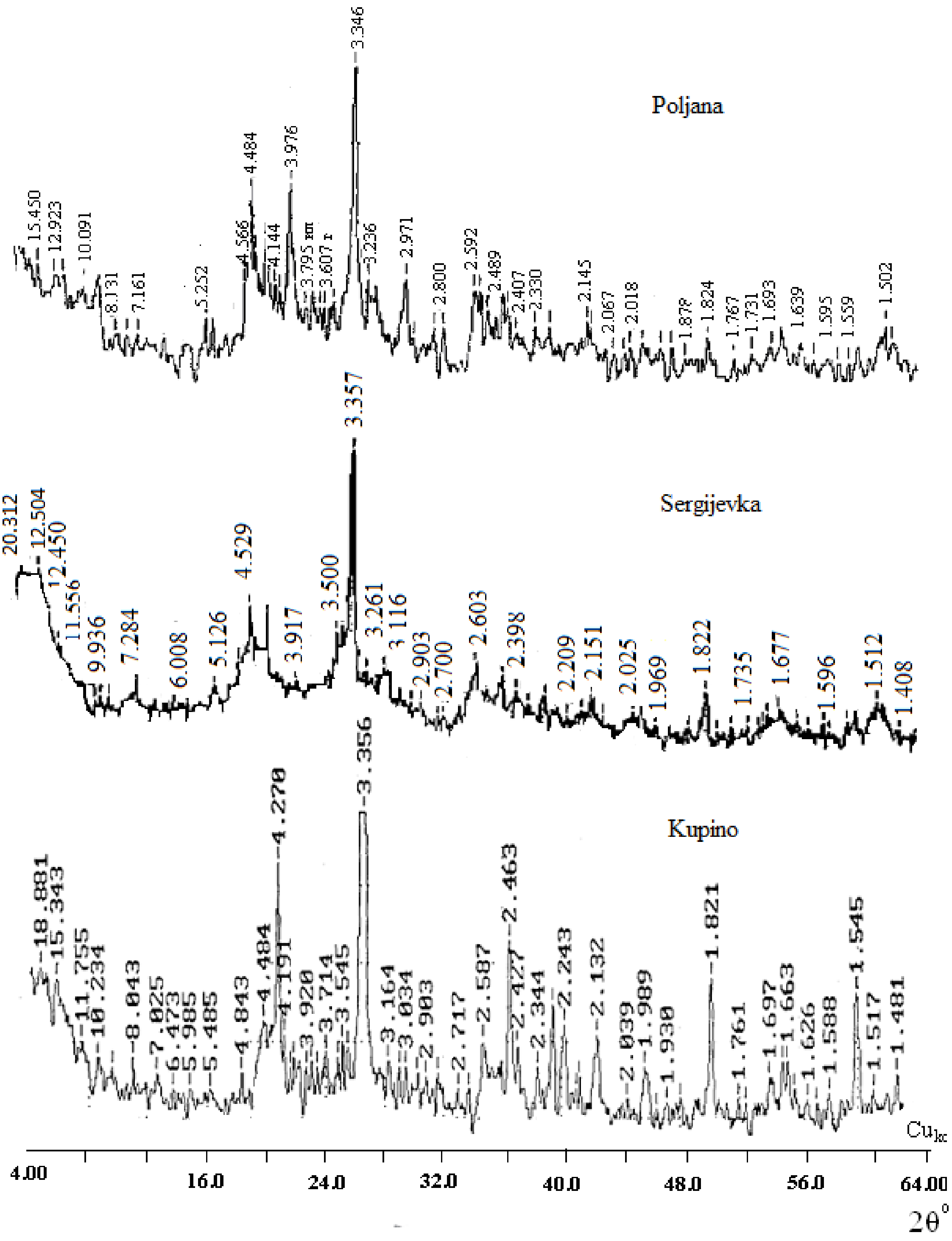


Fig. 2. X-ray powder diffractograms of clays

The mineralogical composition of Kupino clay is represented by: montmorillonite (15.343; 11.755; 5.485; 4.844; 3.545; 3.496; 3.356; 2.903; 2.587; 2.132; 1.989; 1.69; 1.517 Å), quartz (4.270; 3.356; 2.285; 1.821; 1.672; 1.650; 1.609; 1.543 Å), illite (5.485; 3.356; 2.903; 2.463; 1.650; 1.517 Å), kaolinite (7.025; 4.843; 3.584;

2.243; 1.854; 1.663 Å), calcite (3.034; 2.285, 1.626; 1.609; 1.508 Å), and feldspars (3.920; 3.164; 2.835; 2.658 Å).

It was found that high sorption properties of Sergijevka and Poljana clays are consistent with the presence in their composition of a relatively large number of montmorillonite as a sorption-active mineral. In the Poljana clay samples its content (% by weight) was 49.8 - 50.1% (mean 49.9%) [10]. The content of montmorillonite in Sergijevka clay samples was about the same and amounted to 47-52% (mean 49.5%) [11]. The share of montmorillonite in clay of Kupino mineral occurence is significantly lower an amounted to 40 - 45% (mean 42.5%) [12]. Accordingly, the sorption capacity of the last clay is lower than for clays of Poljana and Sergijevka deposits.

Table 1 represents the chemical composition of clays under study. The chemical analysis (Table 1) shows that the tested natural clays differ slightly in content of oxides.

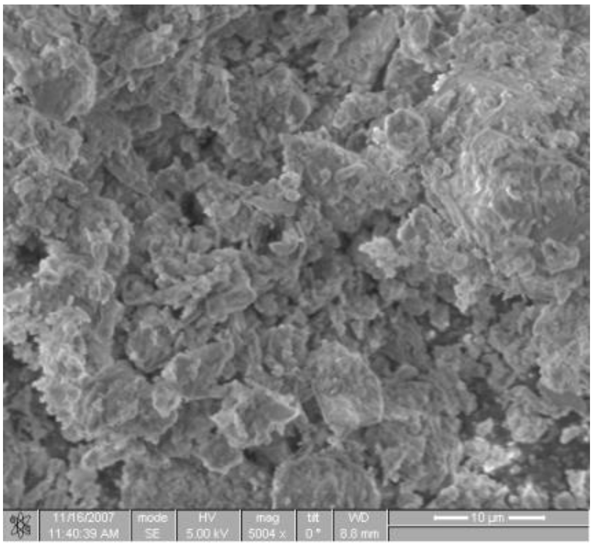
Table 1: The chemical composition of natural clay, % wt

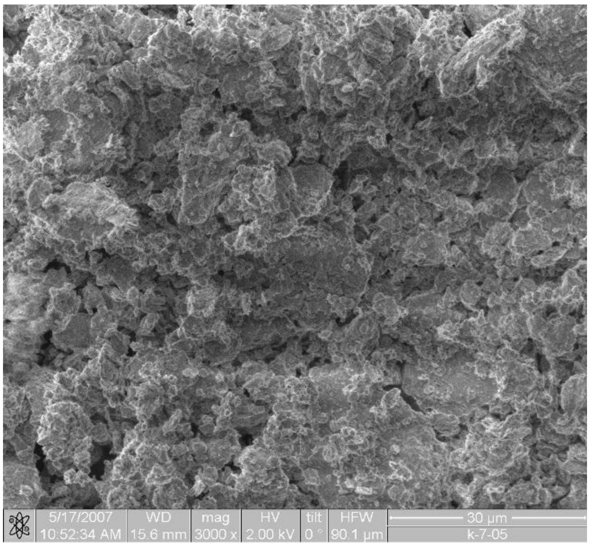
Component percentage, % wt.	Sample		
	Poljana	Sergievka	Kupino
SiO_2	61.60-61.73	61.35-61.50	66.78-67.14
Al_2O_3	12.30-12.40	16.95-17.02	12.03-12.16
Fe_2O_3	3.68-3.73	5.74-5.83	7.87-8.23
TiO_2	0.69-0.70	0.91-1.11	0.70-0.72
MgO	2.25-2.27	1.76-1.93	1.30-1.36
CaO	4.63-4.68	0.85-0.86	1.80-1.83
K_2O	1.76-1.81	2.35-2.43	1.90-1.92
Na_2O	0.64-0.66	0.23-0.29	0.25-0.27
LOI	11.80-12.10	9.94-10.02	7.08-7.29
Σ,%	99.35-100.08	100.08-100.99	99.71-100.92

The higher content of Na_2O in the Poljana clay sample characterizes presence of montmorillonite with a predominance of Na^+ ions in the inter-block positions, and a higher content of calcium oxide indicates the calcium phase of montmorillonite with a share of calcite in the sample.

Figure 3 shows electron micrographs of clays under study.

a)





b)

Fig. 3. Electron micrographs of the clays: a) Poljana; b) Kupino

SEM-photos of Poljana clay show both individual particles the size of which is from 0.1 to 6 mm, and aggregates with size of 10 - 25 mm (Figure 3,a) [9]. In Sergijevka clay there are visible individual particles ranging in size from 0 to 6.6 micron, and 9-16 micron size aggregates [11]. Individual particles in Kupino clay differ slightly from those in Sergijevka clay (Fig. 3b). Most of them have a size of 3-5 mm, but there are also smaller particles with a size of few fractions of microns. However, the maximum size of the aggregates (25 m) in Kupino clay is much higher [12]. Coarsening and aggregation of particles leads to a decrease of the specific surface of the sorbent and thus to reduce in its sorptive capacity, as shown above.

Data on particle size are summarized in Table 2 which also indicates the values of electrokinetic potential for clays under study.

Table 2 shows that the electrokinetic potential of clays is negative, but it differs for various clays by absolute value. Zeta potential of Poljana clay in absolute terms significantly higher than for Kupino and Sergijevka clays.

Table 2: Is colloidal-chemical properties of under study clay

Item. no	Clay	Particle size, mcm		Zeta - potential, mV
		Individual particles	Aggregates	
1	Poljana	0.3 -6	10 - 23	-32.1
2	Sergievka	0.6 - 6	9 - 16	-18.7
3	Kupino	3-5	10-25	-17.3

As a result, we should observe a strong attraction of lead (II) cations from the solution to the surface of sorption-active minerals composing Poljana clay deposits.

The negative zeta potential of Kupino clay has a lower absolute value as compared with Sergijevka clay, and especially, with Poljana clay. The smaller the absolute value of the negative charge of the surface, the fewer the number of positively charged lead (II) ions it draws, therefore, decrease in the clay sorption capability can be expected. This is consistent with the results previously given for definition of sorption capacity which is less for Kupino clay than that for Poljana and Sergijevka.

CONCLUSION

The research carried out has allowed to establish that the rate of sorption of lead (II) cations from aqueous solutions by clayey mineral sorbents is maximal at the initial stage due to the attraction of cations to the negatively charged surface of the clayey minerals. The rate of the process at an initial stage and sorption capacity of Poljana clay exceeds that for Sergijevka clay, however, concedes to it by an average rate of the process. Clays of those deposits have advantages over Kupino clay both in the kinetics of the process and in the sorption capacity. This is due to differences in their chemical and mineralogical composition and colloid-chemical properties, mainly higher content of sorption active mineral (montmorillonite) in Poljana clay and higher absolute negative values of an electrokinetic potential. By the efficiency of water purification from lead (II) ions charcoal concedes to clays of Poljana and Sergijevka deposits. Active carbon is superior than clay sorbents, but it may not be recommended because of its high cost. Most environmentally and cost-effective sorbents for water purification from lead (II) ions are available natural materials: clays from Poljana and Sergievka.

RESUME

In order to determine the practical suitability of montmorillonite-containing clay from few deposits and mineral occurrences of the Belgorod region, charcoal and activated carbon for water purification from lead (II) ions we have carried out a comprehensive analysis of the sorbents that included the definition of process kinetics and sorption capacity. The sorption capacity of the sorbents under study was 0.071 - 0. 081 mg / g. The efficiency of purification from Pb 2+ of aqueous solutions containing 5 mg / l of lead ions (II) by using clay from different deposits and mineral occurrences was up to 85.2 - 90.8 % wt, the charcoal - 88.4 % wt, and activated carbon - 97.6 % wt. An explanation of the results was given on the basis of chemical and mineral composition and colloidal-chemical properties of the sorbents under study.

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