Chemistry

COMPOSITE SORBENTS BASED ON DIATOMITE-BENTONITE AND PAPER-PULP FOR THE REMOVAL OF HEAVY METALS

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The sorption properties of organomineral composite sorbents have been investigated by ICP-MS method. The diatomite of the Jradzor deposit and bentonite of the Sarigyuh deposit (Armenia) were used as inorganic constituents. Diatomite serves as a structure-forming component and provides mass transfer due to its high porosity ($V = 2.0\ cm^3/g$) and large pore sizes (150–200 nm). Bentonite is responsible for the functionality of the sorbents. The organic component is also responsible for the functionality of the obtained sorbents. Paper pretreated with acids (nitric and phosphoric) was used as an organic component. A synthetic solution containing cations of heavy metals was used as an object of study. The experiments were carried out in static mode on a Jar-Test device.

Introduction. An environmental impact assessment is required during and after mine production. If such an assessment procedure is not carried out effectively, deposits with a high content of pyrite (FeS_2) can be sources in the mining industry and on construction sites of large amounts of heavy metals and radionuclides that can be released from solid phases in various weather conditions as a result of precipitation. As a result, they become very mobile. Acid fluxes from sulfide rocks significantly increase the metal content (heavy metals, radionuclides, microelements) in aqueous systems [1]. In addition, trace elements can be present in various forms, from molecular dissolved state to colloid and micron-sized particles. Low molecular weight forms are very mobile [2].

Natural calcium carbonate or lime in the ores delays the hydrolysis of S^{2-} and further solubility of cations [3]. The most common water pollutants are Ca, Mg, Cu, Fe, Pb, Ni, Al, B, C and the radionuclides ^{238}U, ^{130}Ba, ^{137}Cs, ^{90}Sr, ^{60}Co. There are many alternatives for the treatment of wastewater streams. The main methods for removing heavy metals are: Reagent, Membrane, Electrochemical, Biochemical and Sorption methods [4–6].

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The most common and effective method for heavy metals removal is sorption method. The advantage of this method is that it is possible to purify wastewater that contains a large number of impurities (for example, organic or inorganic). The efficiency of water treatment using this method can increase up to 80–95%, depending on the chemical nature of the sorbents, their structure and the size of the absorption surface. In recent years, for water purification, much attention has been paid to natural sorbents or sorbents based on materials of natural origin.

Natural sorbents are widely used due to their low price. The cost of natural sorbents is ten times less than the cost of artificial sorbents. Clay materials are the most common inorganic sorbents that are widely used in water purification. Many natural minerals (for example, zeolites, clays, peat, etc.) have a number of characteristic advantages listed above. For this reason, they are widely studied [7–10]. Selectivity is one of the biggest problems in these minerals. There are several methods to increase selectivity, for example, with respect to the group of systems Cs and Sr. Among them, the most widely used methods are the treatment with acids and alkalis, hydrothermal treatment, and thermal and mechanical activation [11].

In the last few years, a chemically modified carrier has been proposed with specific organic compounds that show selectivity for ions. The carrier can be ion exchange resin, cellulose, activated carbon, natural minerals. The application of this method has led to the development of several new sorbents [12, 13].

Cellulose is the most common biopolymer in the world and the presence of several hydroxyl groups in the structure of its molecules allows modifying its surface properties with the introduction of several chemical groups. Cellulose and its derivatives are used as an adsorbent to remove several contaminants. After chemical modification, cellulosic materials exhibit new properties that are more effective than the starting materials. These new modifying groups on the surface of cellulose increase the interaction with pollutants (metals, dyes, drugs, etc.) during absorption from an aqueous medium, which strongly depends on the pH of the solution. Cellulose materials modified by various groups are promising for use in the removal of pollutants from the aquatic environment.

These chemical modifications form covalent bonds through the interaction between modifying agents and the interactive center of the solid surface [14].

Cellulose derivatives have various applications in various fields. Among the various possibilities is the production of cellulose derivatives to remove contaminants from the aquatic environment. For example, to remove Cu(II) and Pb(II) [15].

Phosphating of cellulose allows the chemical inclusion of phosphorus into the structure of cellulose that changes its properties and the synthesized biomaterial begins to show the characteristics of the phosphate group. Phosphoric acid (H_3PO_4), phosphorus is the main precursor used in the phosphating of cellulose. Depending on the conditions of the phosphating reaction, different products are obtained [16].

Experimental Part. The purpose of this article is to study the sorption of certain heavy metals and radionuclides in a static mode on organomineral composite sorbents.

Materials and Methods.

Obtaining Porous Carrier DB-12P. In all experiments, DB-P was used as a porous carrier (see Tab. 1). The preparation of DB-12P is carried out according to

the following scheme. Bentonite is pretreated with phosphoric acid by keeping it in phosphoric acid for several days, then diatomite is added and the resulting mass is washed to neutral wash water. The use of diatomite is aimed at improving the mass transfer of the resulting sorbent.

Table 1

Sorption data of obtained composite sorbents

t^*	C^{**}	DB-12P													
		K	Ca	Mn	Co	Ni	Cu	Zn	As	Sr	Mo	Cd	Ba	Pb	U
		0.35	0.11	0.55	0.25	0.34	0.79	1.7	1.5	10	0.14	0.0021	0.44	1.7	0.34
		g/L	g/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
15		0.35	0.054		0.21	0.24	0.15	0.15	0.22	3.1	0.10	0.000073	0.024	0.080	0.31
30		0.33	0.052	0	0.20	0.25	0.26	0.26	0.23	3.0	0.099	<LD	0.027	0.050	0.31
60		0.31	0.048	0.10	0.18	0.23	0.20	0.21	0.22	3.1	0.098	0.00014	0.028	0.050	0.31
180		0.30	0.046	0.10	0.18	0.22	0.29	0.30	0.23	2.8	0.10	0.00021	0.033	0.058	0.30
		DB-12P-P													
5		0.007	0.23	9.4	0.11	1.1	0.35	0.41	3.4	6.3	0.053	0.00027	0.14	0.0038	0.053
15		0.001	0.05	1.3	0.00074	0.23	0.022	0.02	0.0065	1.5	0.0016	0.000037	0.045	0.0012	0.0076
30		0.004	0.12	2.9	0.0005	0.50	0.042	0.037	0.0074	3.5	0.0031	0.000078	0.096	0.0025	0.015
60		0.0045	0.13	2.7	0.00026	0.44	0.035	0.046	0.0054	3.5	0.019	0.000066	0.063	0.0022	0.012
180		0.0054	0.12	2.3	0.00093	0.40	0.052	0.065	0.0025	3.5	0.0002	0.000052	0.056	0.0023	0.012
		DB-12P-N													
5		0.010	0.68	6.5	0.094	1.0	0.041	0.061	3.7	6.0	0.54	0.00022	0.018	0.0020	0.0005
15		0.0093	0.68	5.8	0.081	0.97	0.036	0.027	3.6	5.8	0.53	0.00012	0.0096	0.0018	0.0008
30		0.0096	0.54	4.4	0.061	0.76	0.081	0.12	2.8	4.4	0.41	0.00021	0.012	0.0022	0.0005
60		0.0056	0.26	12	0.14	1.3	0.27	0.19	4.1	7.8	0.064	0.00024	0.12	0.0025	0.052
180		0.0051	0.22	9.0	0.11	1.0	0.17	0.16	3.4	6.2	0.052	0.00020	0.078	0.0021	0.025

t^* – exposition time, *min*; C^{**} – initial concentration.

Obtaining Porous Carrier DB-12P-P. First, a pulp is prepared by dispersing 4 *g* of paper in H_3PO_4, heated, held out for 2–3 *h*, then 180 *mL* of water is added, followed by heating to boiling with constant stirring for 30–40 *min*. Next, 50 *g* of DB-12P is mixed with 80 *mL* of paper pulp with stirring to obtain a homogeneous mass. The resulting mass is dried at 150°C.

Obtaining Porous Carrier DB-P-N. The crushed pulp is incubated in 10 *mL* of conc. HNO_3 over 2 *min*, then water is added to 80 *mL* and with stirring 50 *g* of DB-12P is added. As a result, a homogeneous pasty mass is obtained, which is dried at 105°C to a dry state. Next, the resulting mass is crushed to a powder.

Results and Discussions. Fig. 1 shows the dependence of the relative adsorption of Pb on DB-12P, DB-12P-P and DB-12P-N sorbents. The equations of these dependencies are functions of the relative adsorption – C/C_0 dependence on the sorbent exposure time in the test solution, i.e., the equation describes how C/C_0 values change over time. Using these equations, the maximum adsorption value was determined according to the method described below.

The bases of this model can be presented under the following assumptions. It is well known that the amount of the adsorbed substance is calculated by the following formula:

$$q = V(C_0–C)/m, \tag{1}$$

where C_0 is the initial concentration in d/L; C is the equilibrium concentration, g/L; V is the volume of solution, L; m is the mass of the sorbent, g. Converting (1), we get the following:

$$q/C_0 = V/m(C_0–C)/C_0,$$
$$q/C_0 = V/m\ (1–C/C_0), \tag{2}$$
$$q = VC_0/m\ (1–C/C_0).$$

In this case, consider changing of C/C_0 as a function of time (time of exposure of the sorbent in the solution) (Tab. 2). To do this, the value of C is measured at regular intervals and a curve established equilibrium concentration from time is constructed by formula of this relationship using Excel Trendline, the value q is determined by placing the value C/C_0 in the Eq. (2).

$$q = VC_0/m\ [1–C/C_0(t)]. \tag{3}$$

Another important aspect of Fig. 1 is that it can be used to judge whether adsorption is completed or not. This is very important for a real assessment of the sorption capacity of the sorbent.

As it follows from Fig. 2, the change in functional groups has practically no effect on the sorption properties of Pb. Apparently, the mechanism of Pb sorption on these sorbents is of the same nature and does not depend on the functional groups brought with the help of modified paper components. It is assumed that the first priming structuring in DB-P during acid treatment of bentonite causes sorption of Pb and the introduction of a paper component into the composition of this sorbent does not lead to any change in the sorption capacity of the obtained sorbents, i.e., the paper component does not play any role in changing the sorption of Pb.

From Tab. 3 and Fig. 3 the values of the sorption capacity of the above mentioned sorbents were calculated (see Fig. 4). It follows from Fig. 4 it follows that the largest sorption capacity has the initial sorbent DB-12P. This apparently indicates that the primary structure of the initial sorbent becomes decisive in the sorption of Ba. The paper component does not affect the sorption, and even vice versa, it becomes ballast, which causes a decrease in the sorption capacity of paper-containing sorbents. It is remarkable that the sorption capacity of sorbents containing paper is almost the same. This fact shows once again that paper and functional groups on its surface do not affect the sorption properties of sorbents. From this point of view, the sorption mechanism of Ba looks strange, since if we assume that cation-exchange is the main one in this mechanism, then this would mean that functionalized paper, for example, with phosphoric acid, does not participate in the sorption processes of Ba. Hence the conclusion that the main thing in adsorption is the structuring of the primary sorbent under the influence of phosphoric acid on bentonite.

Due to the fact that arsenic is one of the most toxic elements found in wastewater and other environmental matrices, the development of sorbents for the extraction of arsenic is an important task. In addition, an important issue is the very low residual concentrations of As. Obtaining sorbents for sorption of extremely low concentrations and bringing them up to 95% or more is not an easy task. From this point of view, DB-12P, DB-12P-P and DB-12P-N sorbents meet these requirements.
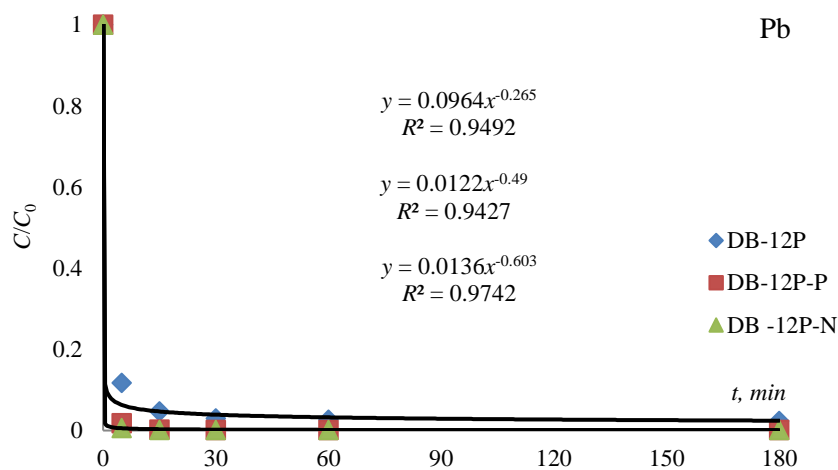
Fig. 1. Dependence of relative adsorption (C/C_0) of Pb on the exposure time of DB-12P, DB-12P-P and DB-12P-N sorbents in solution.
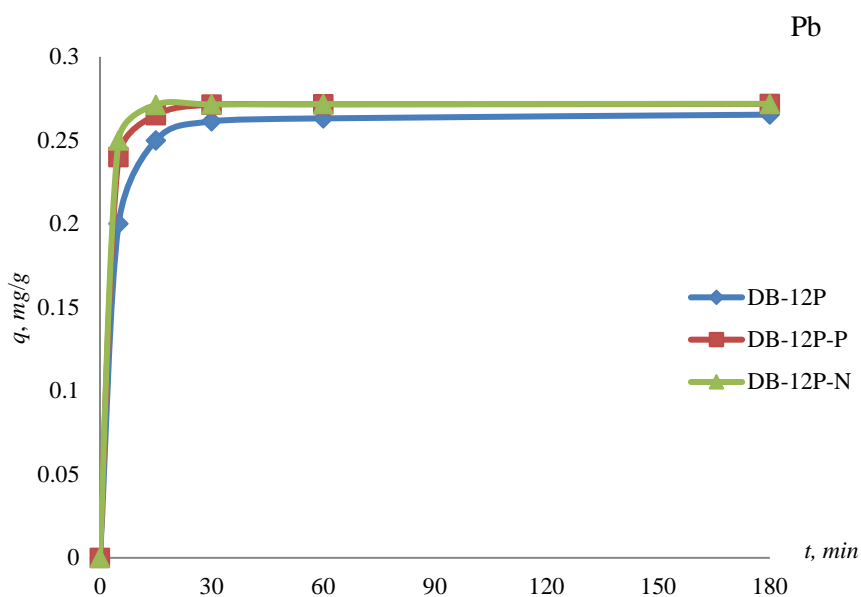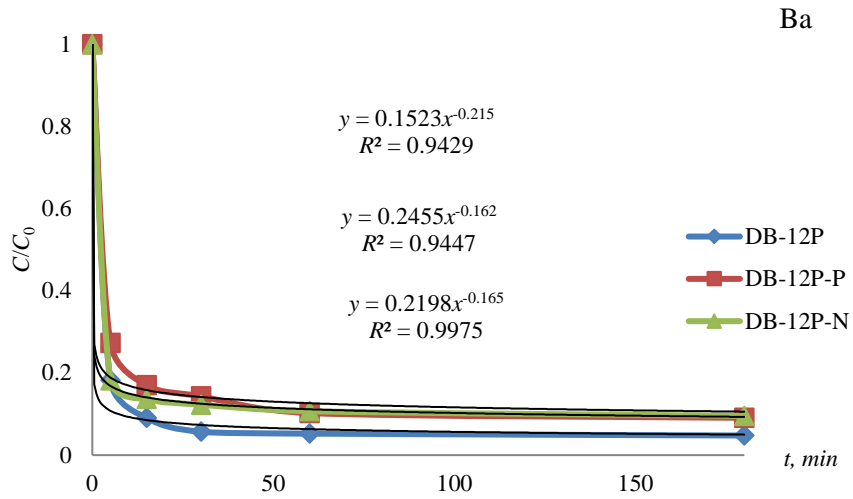
In the figure:

$y = 0.0964x^{-0.265}$
$R^2 = 0.9492$

$y = 0.0122x^{-0.49}$
$R^2 = 0.9427$

$y = 0.0136x^{-0.603}$
$R^2 = 0.9742$

Fig. 2. Absorption capacity of DB-12P, DB-12P-P and DB-12P-N sorbents by Pb.

Table 2

The change in the values of the relative sorption of Pb in time

Sorbent	Equation	R^2
DB-P	$C/C_0 = 0.0964\, t^{-0.265}$	0.9492
DB-P-P	$C/C_0 = 0.0122\, t^{-0.49}$	0.9427
DB-P-N	$C/C_0 = 0.0136\, t^{-0.603}$	0.9742

Fig. 3. Dependence of relative adsorption (C/C_0) of Ba on the exposure time
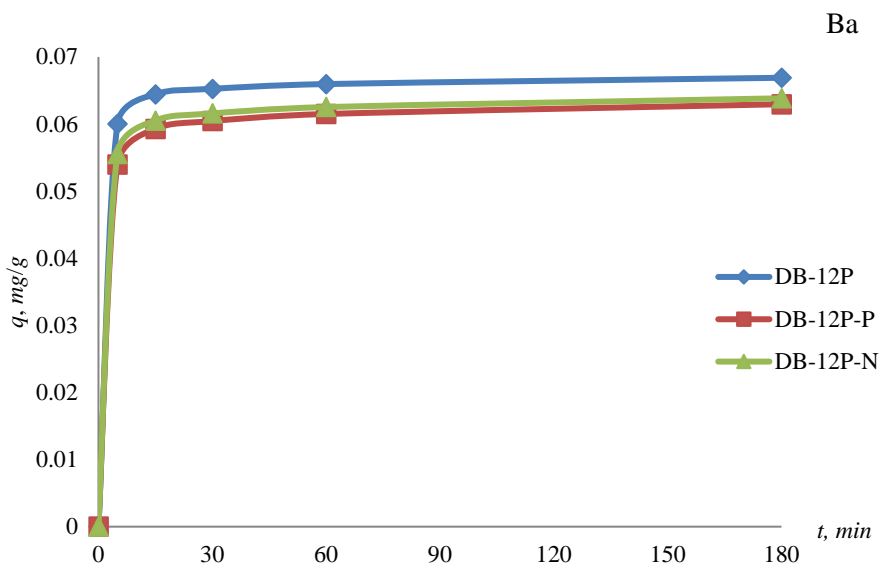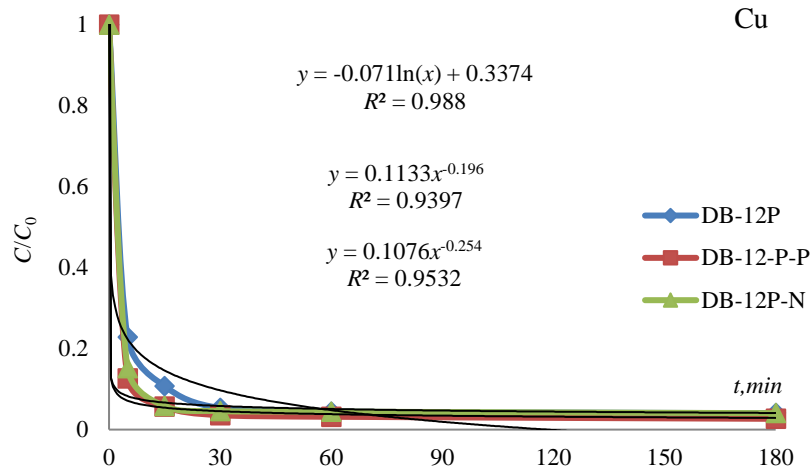of DB-12P, DB-12P-P and DB-12P-N sorbents in solution.

Fig. 4. Adsorption capacity of DB-12P, DB-12P-P and DB-12P-N sorbents by Ba.

T a b l e   3

The change in the values of relative sorption of Ba in time

Sorbents	Equation	R^2
DB-P	$C/C_0 = 0.1523t^{-0.215}$	0.9429
DB-P-P	$C/C_0 = 0.2455t^{-0.162}$	0.9447
DB-P-N	$C/C_0 = 0.2198t^{-0.165}$	0.9975

Fig. 5. Dependence of relative adsorption (C/C_0) of Cu on the exposure time of DB-12P, DB-12P-P and DB-12P-N sorbents in solution.
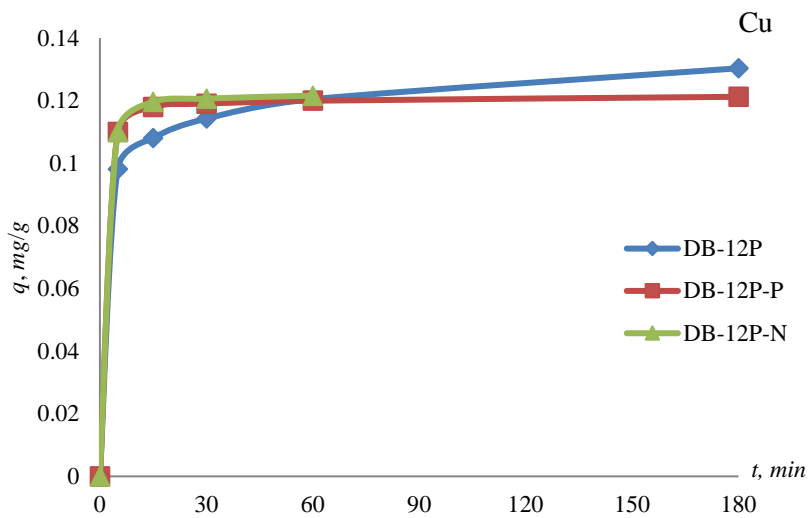

Fig. 6. Absorption capacity of sorbents DB-12P, DB-12P-P and DB-12P-N by Cu.

Table 4

The change in the values of the relative sorption of Cu in time

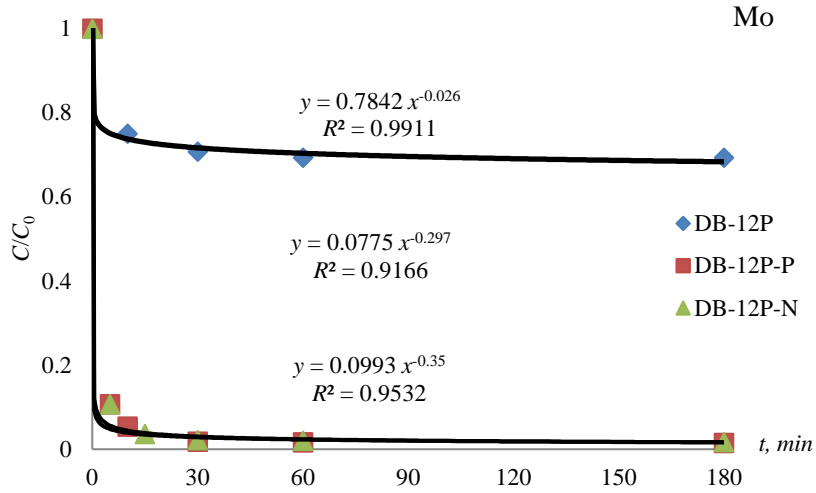| Sorbent	Equation	R^2
DB-P	$C/C_0 = -0.071\ln(x) + 0.3374$	0.9880
DB-P-P	$C/C_0 = 0.1133x^{-0.196}$	0.9397
DB-P-N	$C/C_0 = 0.1076x^{-0.254}$	0.9532

Fig. 7. Dependence of the relative adsorption (C/C_0) of Mo on the exposure time
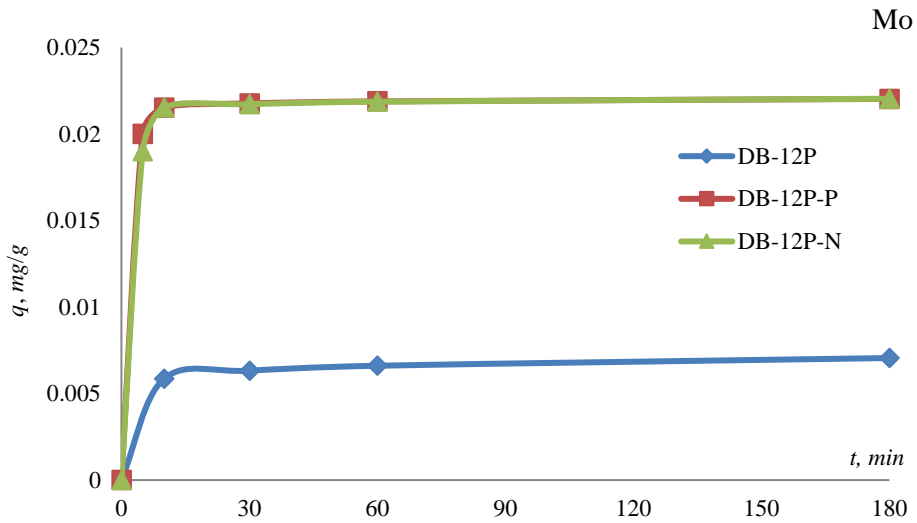of DB-12P, DB-12P-P and DB-12P-N sorbents in solution.

Fig. 8. Absorption capacity of DB-12P, DB-12P-P and DB-12P-N sorbents by Mo.

T a b l e   5

The change in the values of the relative sorption of Mo in time

Sorbent	Equation	R^2
DB-P	$C/C_0 = 0.7842\,x^{-0.026}$	0.9911
DB-P-P	$C/C_0 = 0.0775\,x^{-0.297}$	0.9166
DB-P-N	$C/C_0 = 0.0993\,x^{-0.35}$	0.9532

As follows from Figs. 5, 6 and Tab. 4 the introduction of a modified paper component into the sorbents does not lead to an increase in the adsorption of Cu.

The sorption of Mo is significantly improved with the introduction of the paper component into the composition of the sorbent DB-12P, and the type of paper modification does not matter for sorption. In both cases, they coincide, so if the sorption capacity of the initial DB-12P Mo sorbent is 0.006 *mg/g*, then for sorbents containing paper with different functional groups in their composition, this value is 4 times higher and is about 0.022 *mg/g* (see Figs. 7, 8 and Tab. 5).

Conclusion. It has been that by introducing a functionalized paper component into a porous carrier obtained from bentonite-diatomite mixture, sorbents are obtained that adsorb heavy metals from water. The functionalization of the paper component is carried out by treating the paper pulp with phosphoric and nitric acids. Diatomite serves as a structure-forming component and provides mass transfer due to its high porosity and large pore sizes. Bentonite is responsible for the functionality of the sorbents as well.

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ԴԻԱՏՈՄԻՏ-ԲԵՆՏՈՆԻՏԻ ԵՎ ՑԵԼՅՈՒԼՈԶԻ ՀԻՄԱՆ ՎՐԱ
ԿԱԶՄՎԱԾ ԿՈՄՊՈԶԻՑԱՅԻՆ ՍՈՐԲԵՆՏՆԵՐ ԾԱՆՐ ՄԵՏԱՂՆԵՐԻ
ՀԵՌԱՑՄԱՆ ՀԱՄԱՐ

ICP-MS եղանակով հետազոտվել են օրգանահանքային կոմպոզի-տային սորբենտների սորբցիոն հատկությունները: Որպես անօրգանական բաղադրիչներ օգտագործվել են Ջրաձորի հանքավայրի դիատոմիտը և Սարիգյուղի հանքավայրի բենտոնիտը (Հայաստան): Դիատոմիտը ծառայում է որպես կառուցվածք առաջացնող բաղադրիչ և ապահովում է զանգվածա-փոխանակությունը՝ բարձր ծակոտկենության (V = 2,0 սմ³/q) և ծակոտիների մեծ չափերի (150–200 նմ) շնորհիվ: Բենտոնիտը պատասխանատու է սորբենտների ֆունկցիոնալության համար: Օրգանական բաղադրիչը նույնպես պատասխանատու է ստացված սորբենտների ֆունկցիոնալության համար: Թթուներով (ազոտական և ֆոսֆորական) մշակված թուղթն օգտագործվում էր որպես օրգանական բաղադրիչ: Որպես հետազոտության առարկա օգտագործվել է ծանր մետաղների կատիոններ պարունակող սինթետիկ լուծույթը: Փորձերն իրականացվել են ստատիկ ռեժիմով՝ Jar-Test սարքի վրա:

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КОМПОЗИЦИОННЫЕ СОРБЕНТЫ НА ОСНОВЕ ДИАТОМИТА-БЕНТОНИТА И ЦЕЛЛЮЛОЗЫ ДЛЯ УДАЛЕНИЯ ТЯЖЕЛЫХ МЕТАЛЛОВ

Методом ICP-MS исследованы сорбционные свойства органоминеральных композиционных сорбентов. В качестве неорганических компонентов использовали диатомит Джрадзорского месторождения и бентонит Сарыгюхского месторождения (Армения). Диатомит служит структурообразующим компонентом и обеспечивает массоперенос за счет высокой пористости ($V = 2{,}0$ $см^3/г$) и больших размеров пор (150–200 $нм$). Бентонит отвечает за функциональность сорбентов. Органический компонент также отвечает за функциональность получаемых сорбентов. В качестве органического компонента использовалась бумага, обработанная кислотами (азотной и фосфорной). В качестве объекта исследования применялся синтетический раствор, содержащий катионы тяжелых металлов. Эксперименты проводились в статическом режиме на приборе Jar-Test.