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Experimental studies of organic matter in natural waters of lakes in Vladimir region using a set of analytical methods.

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Abstract. Organic matter in natural waters takes an active part in the migration of trace elements, playing a crucial role in the biogeochemical cycles of trace elements. The paper discusses the results of research on the organic matter of natural waters of lakes in Vladimir region, obtained using a set of analytical methods. Selected as objects of the study were representative waterbodies with different levels of primary productivity: eutrophic lake Ershevik, dystrophic lake Ignatkovo. The proposed set of analytical methods for determining the content, composition and forms of finding organic matter and related trace elements includes determining the content of dissolved organic carbon and N on the liquid element analyzer LiquiTOC trace, Elementar; studying the molecular mass distribution of organic matter by high-performance liquid chromatography in a variant of gel-penetrating chromatography; studying the forms of finding organic matter and trace elements by cascade filtration with the separation of size fractions; spectrophotometric measurement of water density using a Specord 50 (ANALYTIK JENA) and 511 UV/Vis (Portlab) spectrophotometer to study the absorption spectra of samples in the UV and visible regions of the spectrum, followed by the calculation of indicators that characterize the dissolved organic matter, the degree of its humification, the proportion of autochthonous and allochthonous organic matter.

Keywords: organic matter; natural waters;complex of analytical methods.

The aim of the research was to study, typify and carry out a comparative analysis of the organic matter in natural waters of the lakes of Vladimir Oblast. Identification of regional and local differences in the migration of ionic forms, organic complexes, and suspensions in natural waters is of great practical importance for prognostication and justification of quantitative models of river runoff evolution under the influence of various natural and anthropogenic factors. To obtain information on sustainable correlations between microelements and organic matter, as well as the mechanisms of their concerted transport and deposition in various natural conditions, as objects of study we chose reservoirs with different levels of primary productivity: the eutrophic Lake Ershevik and the dystrophic Lake Ignatkovo in Vladimir Oblast in the drainage basin of the Klyazma River. The water of Lake Ershevik is characterized by near neutral pH values of about 7, while in Lake Ignatkovo pH is equal to 5.7. Lake Ershevik had higher indices of chromaticity, permanganate oxidizability and BOD_5: chromaticity of -179 degrees of Cr-Co scale; permanganate oxidizability of 20 mg O_2/dm^3; biological oxygen demand of 2 mg O_2/dm^3.

Organic matter in natural waters takes an active part in the processes of migration of trace elements, playing a decisive role in the biogeochemical cycles of trace elements. The work discusses the results of studying the organic matter in natural waters of the lakes of Vladimir Oblast obtained using a complex of analytical methods. As objects of study, representative water bodies with different levels of primary productivity were selected: the eutrophic Lake Ershevik and the dystrophic Lake Ignatkovo. Separately, we analyzed the waters of the surface euphotic horizon, the bottom horizon, and silt waters extracted from bottom sediments.

To study the distribution of organic matter and trace elements in natural waters by size fractions and to separate truly dissolved forms of metals from suspended and colloidal particles in natural waters, we applied the method of cascade membrane filtration and ultrafiltration with pore diameters of 0.45 µm, 0.22 µm and 0.014 µm (1 kDa) using an Amicon device, followed by an analysis of the content of a large number of trace elements in the isolated fractions of natural waters by the ICP-MS method (Element 2, Thermo Scientific) (Alekhin, 2010). In samples of natural waters, hydrochemical indices were determined according to standard GOST methods. The proposed complex of analytical methods for determining the content, composition and forms of organic matter and associated trace elements also includes the determination of the content of dissolved organic carbon (DOC) and N on the liquid elemental analyzer LiquiTOC trace (Elementar), spectrophotometric measurement of water density on a Specord 50 spectrophotometer (ANALYTIK JENA) and 511 UV/Vis spectrophotometer (Portlab) to analyze the absorption spectra of samples in the UV and visible regions, and study of the molecular weight distribution of organic matter by high-performance liquid chromatography (specifically, gel permeation chromatography) on an Agilent 1100 chromatograph with a diode array detector. Column: TSK G2000SW 7.5x300 mm. Eluent: 0.1 M phosphate buffer, pH 7 + 0.1% SDS (sodium dodecyl sulfate). Speed: 0.5 ml/min. Sample volume: 50 µl. Based on the results obtained, we calculated indices that characterize the dissolved organic matter, degree of its humification, proportions of autochthonous and allochthonous organic matter.

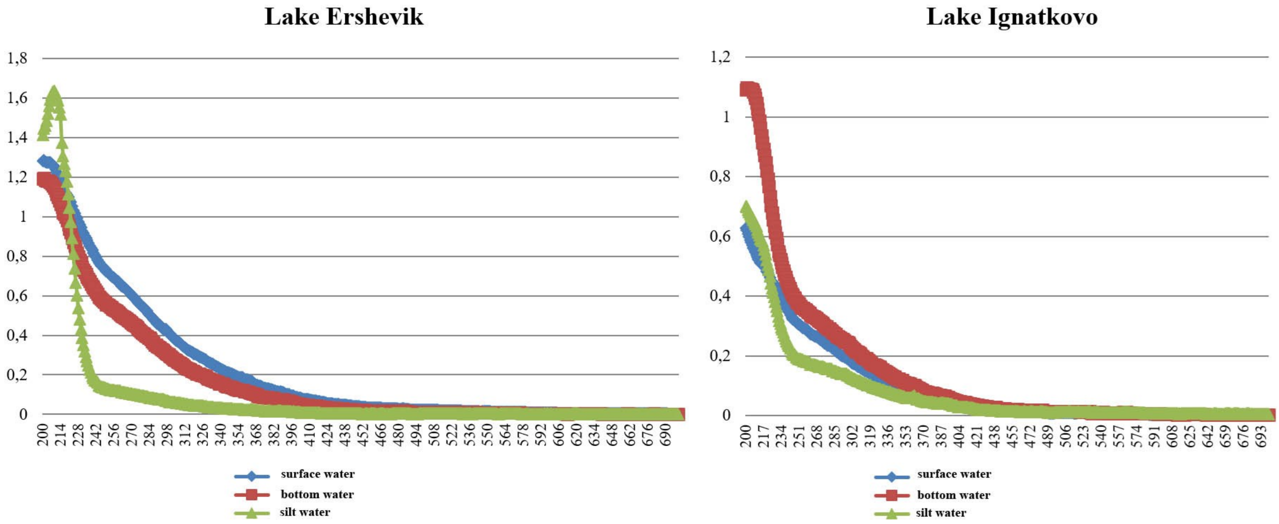

Fig.1. Absorption spectra of dissolved organic matter in natural waters.

Fig.2. Diagrams of the mass distribution of organic matter and trace elements by size fractions of natural waters (for example, oz.Ershevik).

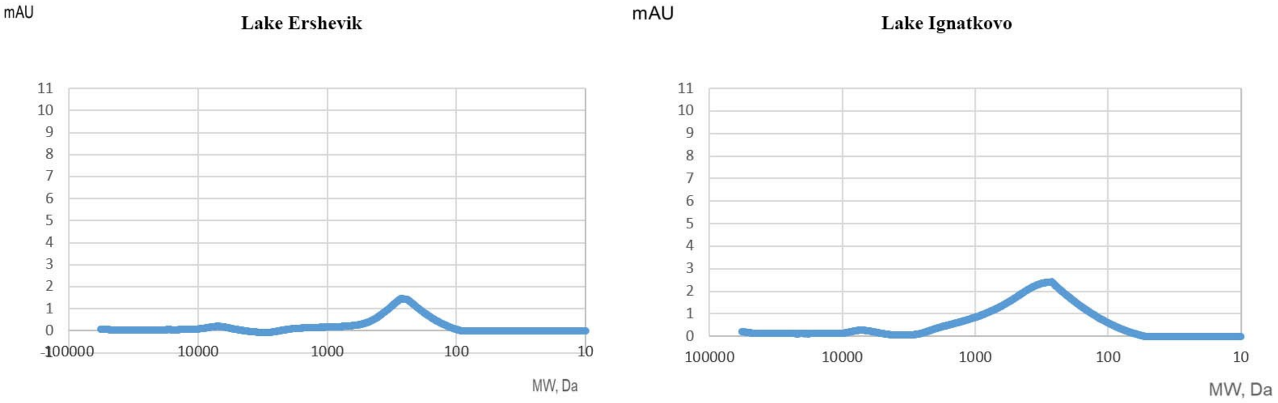

Fig.3. Chromatogram of molecular mass distribution of organic matter of natural waters (filtrate 0.22 μm).

The absorption spectra (Fig. 1) were used to calculate the indices characterizing the dissolved organic matter: SUVA, E_{254}/E_{436}. The SUVA index was calculated as the ratio of the absorption at 254 nm to the content of dissolved organic carbon in the sample (Table 1). The value of SUVA>4 indicates a predominance of hydrophobic and especially aromatic compounds, while SUVA<3 corresponds to predominantly hydrophilic compounds (Edzwaid, Tobiason 1999). The E_{254}/E_{436} ratio is calculated in order to assess the predominance of autochthonous or allochthonous dissolved organic carbon (Battin, 1998). Lake Ershevik had higher values of optical density that correlate with the degree of humification of dissolved organic matter; for Lake Ignatkovo, this index was 2 times lower. The predominant role of the hydrophobic and aromatic fraction in the composition of organic matter is characteristic of Lake Ershevik, especially in the summer, whereas the dystrophic Lake Ignatkovo is characterized by the predominance of the hydrophilic fraction of organic matter. The high values of the E_{254}/E_{436} ratio in Lake Ershevik, especially in the bottom horizon and silt waters, confirm the predominant role of autochthonous organic matter formed as a result of the biogeochemical activity of aquatic plants and plankton inside the reservoir. For the dystrophic Lake Ignatkovo, the indices were found to be lower, which indicates a significant contribution of terrigenous organic matter in the composition of dissolved organic matter.

Table 1. Main characteristics of organic matter of natural waters of lakes of the Vladimir region.

	DOC, mg /l	N, mg /l	E_{254}	E_{436}	C/ N	SUVA	E_{254}/E_{436}
Lake Ershevik							
unfiltered	19.3	1.09	0.868	0.053	18	5	16
surface water (< 0.22 μm)	18.3	0.98	0.698	0.048	19	4	15
surface water (< 1 kDa)	16.5	0.89	0.496	0.021	19	3	24
bottom waters (< 0.22 μm)	16.4	0.97	0.540	0.029	17	3	19
bottom waters (< 1 kDa)	14.7	0.99	0.392	0.013	15	3	30
silt water (< 0.22 μm)	6.6	4.70	0.123	0.005	1.4	2	25
silt water (<1 kDa)	5.7	4.56	0.095	0.002	1.3	2	48
Lake Ignatkovo							
unfiltered	9.9	0.51	0.306	0.019	19.4	3	16
surface water (< 0.22 μm)	9.3	0.39	0.295	0.021	23.8	3	14
surface water (< 1 kDa)	8.8	0.32	0.243	0.011	27.5	3	22
bottom waters (< 0.22 μm)	10.0	1.03	0.36	0.029	9.7	4	12
bottom waters (< 1 kDa)	7.0	0.62	0.179	0.008	11.3	3	22
silt water (< 0.22 μm)	8.7	1.59	0.187	0.018	5.5	2	10
silt water (< 1 kDa)	6.3	0.97	0.114	0.010	6.5	2	11

The study of the distribution of organic matter in natural waters by size fractions indicates the predominance of low molecular weight organic matter (<1kDa), the proportion of which reaches 98% (Fig. 2). Not more than 39% of dissolved organic carbon is represented by a fraction from 0.22 μm to 0.014 μm (1 kDa). The distribution of organic matter and trace elements by fractions is identical for the lakes under study and allows to identify a general pattern of the behavior of trace elements that is characteristic of ecosystems of water bodies in the Central Russia. A comparative analysis of the organic matter in surface waters showed that small lakes are characterized by rather high concentrations of dissolved organic carbon (9-19 mg/L).

The results of the study of the molecular weight distribution of organic substances by HPLC showed that the chromatograms obtained for surface waters are characterized by a monomodal distribution and have an identical form. In the surface waters of both lakes, the composition of organic matter is predominated by low molecular weight organic compounds with average molecular weights M_w=269 Da for Lake Ignatkovo and M_w=258 Da for Lake Ershevik (Fig. 3). Moreover, their concentration in Lake Ignatkovo is significantly higher than that in Lake Ershevik.

The statistical treatment of analytical data by the method of factorial and correlation analysis using the Gold-Geochemist program allowed to identify several groups of elements according to the degree of correlation of their content with the content of dissolved organic carbon, Fe and Mn.

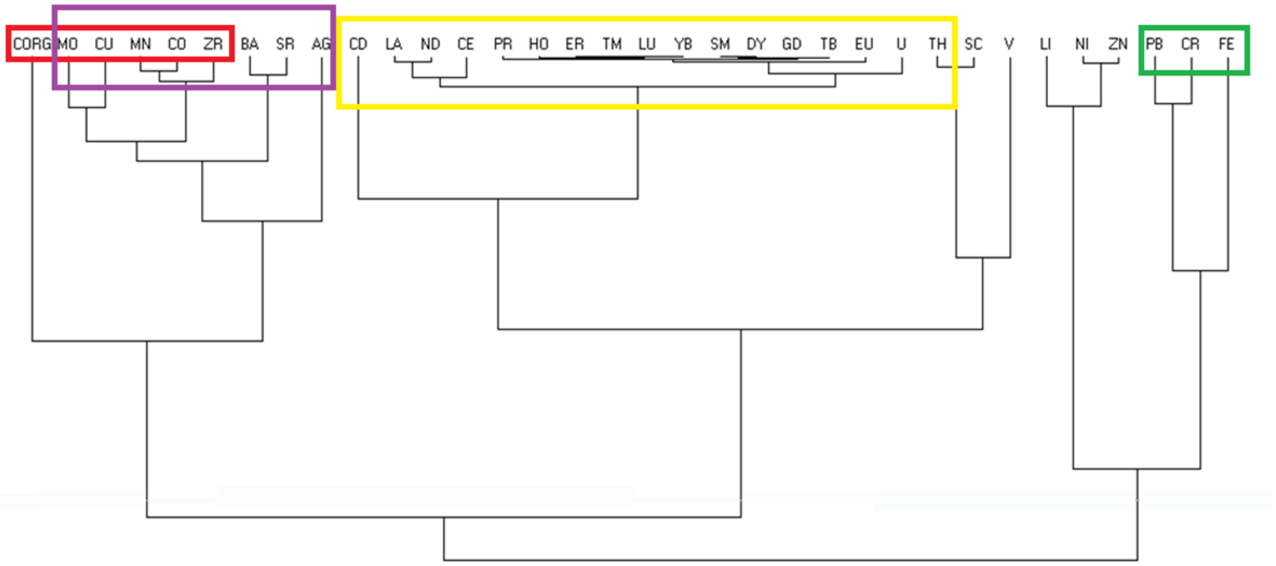

Fig.4. Dendrogram of correlations.

The proposed complex of analytical methods makes it possible to carry out a comprehensive study of the content, composition and forms of organic matter and associated trace elements to identify the patterns of their concerted migration in aquatic ecosystems.

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References

Alekhin Yu. V., Ilina S. M., Lapitsky S. A., Sitnikova M. V. Results of studying the joint migration of trace elements and organic matter in the river flow of the boreal zone// Vestn. Mosk. UN-TA. Ser. GEOL. 2010. no. 6, p. 49-55. In-Rus.

Battin T.J. Dissolved organic materials and its optical properties in a blackwater tributary of the upper Orinoco River, Venezuela. Organic Geochemistry, 28, 1998, - p.561-569.

Edzwald J.K., Tobiason J.E. Enhanced coagulation: US requirements and a broader view. Water Science and Technology, 40, 1999. – p.63-70.

Salavatova D.S., Fiaizullina R.V., Bychkov D.A. Adsorption extraction of mercury ions from an aqueous solution by rocks of the Maykop series. UDC 550.424: 550.4.02: 550.41: 550.42

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Abstract. The behavior of mercury in the mud volcanic process has not been sufficiently studied. Mercury accumulates on clays by adsorption from water, and then desorption occurs and it begins its own behavior in the mud volcanic system. The determination of sorption characteristics for clays of the Maykop series of varying degrees of transformation has become our first priority. In this work, we studied the dependence of mercury adsorption on the pH of the solution and the duration of the contact of the solution with the adsorbent. Experimental adsorption isotherms are obtained, which are analyzed using the equations of Langmuir, Freundlich, Redlich-Peterson, and Toth. It has been shown that the observed adsorption process is described by the Redlich-Peterson and Toth models, which indicates the predominantly chemical nature of adsorption and that the adsorption centers are not identical in their properties.

Keywords *mercury adsorption; mercury in mud volcanoes; adsorption isotherms; Maykop series.*

Mud volcanism is provided by two processes: the process of transformation of sedimentary rocks or the so-called illite-smectite transition, i.e. the conversion of mixed-layer clays with a high water content to hydromica minerals such as illite with a lower water content, the process of water evolution and the sorption properties of clay minerals change: their specific surface decreases and, accordingly, the components that were in the sorbed complex of mixed-layer smectite minerals transfer to the newly formed water. The behavior of mercury under these conditions has not been adequately studied. Mercury accumulates on clays by adsorption from water, and then its desorption occurs and it begins its own behavior in the mud volcanic system. Little is said about the behavior of mercury in the processes of mud volcanism in modern literature. For example, in the work of Portuguese colleagues (Mieiro, Pato et al., 2007), cores of sediments of a mud volcano in the Gulf of Cadiz (Atlantic Ocean, Portugal, Spain) were studied and it was shown that the mercury content in them varied from 9.0 to 86.2 ppb. There are generalized data on the mercury content in the waters of mud volcanoes of the Kerch Peninsula, the North-

West Caucasus, Azerbaijan and Turkmenistan, which ranged from 0.2 to 0.5 ppm, with an average concentration of 0.38 ± 0.19 ppm, calculated on the basis of 10 measurements (Ivanov, 1996). Thus, the aim of this study was to study the sorption properties of clays of the Maykop series of varying degrees of conversion with respect to mercury (II) ions. The laboratory air temperature during all experiments was 25.6±2.3°C. To measure the equilibrium concentration of mercury, the "cold vapor" method was used with an atomic absorption spectrometry using Portable Mercury Analizer PMA-1 (EcON, Moscow) with a PAR-3m attachment. The reducing agent was a 1% sodium borohydride solution in a 1% sodium alkali solution. To control the acidity of the solutions, the Expert-001 pH meter (Econix-Expert, Moscow) was used. As the pH electrode, the EGK-10601 combined glass electrode (Measuring equipment, Moscow) was used. The concentration of adsorbed mercury was determined by the difference in concentrations in solutions according to the equation (Fiaizullina et al., 2020):

$$q_e = \frac{(C - C_e) \cdot m_{sol}}{m_{sorb}}, \quad (1)$$

where q_e is the amount of Hg(II) adsorbed at equilibrium is (ppb); C and C_e are the initial and equilibrium concentrations of metal ions in solution (ppb); m_{sol} is the mass of the solution (g); m_{sorb} is the mass of adsorbent (g). The degree of mercury extraction (E, %) from solutions was calculated by the equation:

$$E = \frac{C - C_e}{C} \cdot 100\% . \quad (2)$$

The effect of pH. It was shown that the maximum adsorption of mercury occurs at pH = 3-4 (Salavatova, Fiaizullina, 2019) and is 240 ppm (E = 99.3%). When discussing changes in the degree of extraction of elements by clays in an acidic environment, the dissolution of clays cannot be ruled out. However, in our opinion, the dissolution of clay components in a medium with pH = 3–4 is unlikely, since the clay samples we study mainly contain clay minerals and quartz, which are highly acid resistant and should not dissolve under these conditions. All experiments described in this work were performed in the range of 3-4 pH units.

Kinetics of adsorption. To study the kinetics of adsorption on clay of the Maykop series of low degree of conversion, two series were delivered: with and without shaking. In a series with stirring, the tubes were shaken manually 3 times a day. The exposure time ranged from 15 minutes to 1 month. Figure 1 shows that after 4 days under dynamic conditions the mercury removal completeness reaches more than 96% - the process reaches equilibrium. Under conditions without shakng, equilibrium occurs only after 2 weeks and persists after a month.

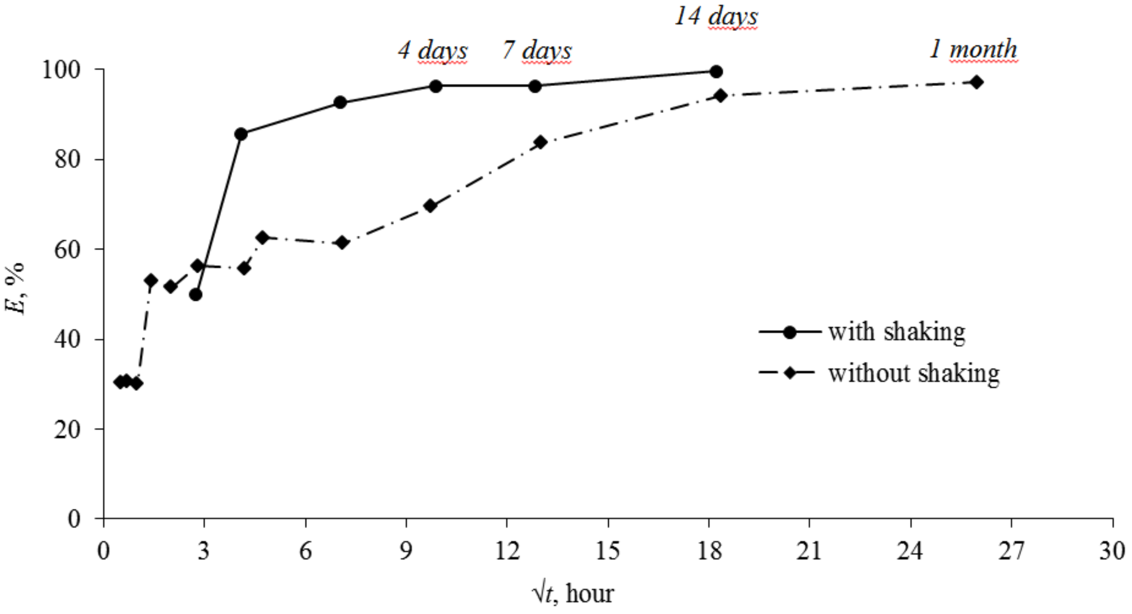

Fig. 1. The degree of mercury extraction over time (there is the square root of time in hours on the abscissa)

Adsorption isotherms. Analysis of adsorption isotherms gives an idea of the features of the adsorption process, the effectiveness of the selected sorbent and allows us to evaluate the feasibility of its use for the absorption of certain substances. In the present work, adsorption isotherms were analyzed using the equations of Langmuir (Langmuir, 1916), Freundlich (Freundlich, 1906), Redlich-Peterson (Redlich, Peterson, 1959), and Toth (Toth, 1971). Traditionally, to find the parameters of equations, their linearized forms are used. However, as shown in (Boulinguiez et al., 2008), it is much more efficient to minimize the nonlinear chi-square test with solver add-in function of the Microsoft Excel. All further results were obtained using this method. The values of the parameters of the equations and the χ^2 are given in table 1. The chi-square test was calculated according to the equation:

$$\chi^2=\sum_{i=1}^{n}\frac{\left(q_e^{calc.}-q_e^{meas.}\right)^2}{q_e^{meas.}}, \qquad (3)$$

where χ^2 is nonlinear chi-square test, q_e^{calc} is calculated adsorbate concentration at equilibrium (mg/g), q_e^{meas} is measured adsorbate concentration at equilibrium (mg/g). Small χ^2 value indicates a good description using the selected adsorption model.

Table 1. The adsorption isotherm parameters calculated using four models and χ^2

Isoterm	Equation	Parameter	Value	χ^2
Langmuir	$q_e = q^\infty \cdot \frac{K_L \cdot C_e}{1+K_L \cdot C_e}$	$q\infty$, mg/g	9.01	2.08
		K_L	0.00147	
Freundlich	$q_e = K_F \cdot C_e^{\frac{1}{n}}$	n	2.08	0.677
		K_F	0.118	
Redlich-Peterson	$q_e = \frac{K_R \cdot C_e}{1+a_R \cdot C_e^g}$	g	0.641	0.241
		a_R	0.113	
		K_R	0.0415	
Toth	$q_e = \frac{K_T \cdot C_e}{\left(a_T + C_e\right)^{\frac{1}{t}}}$	t	1.62	0.208
		a_T	38.3	
		K_T	0.284	

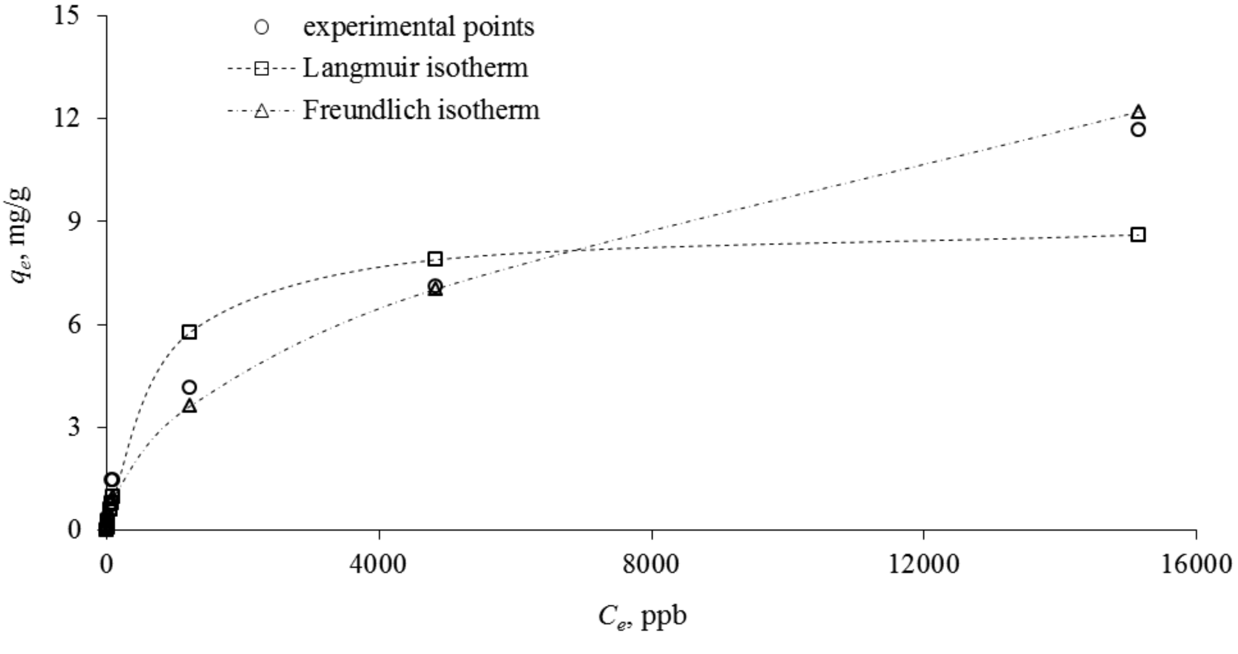

Fig. 2. Isotherms of mercury adsorption on clay of the Maykop series calculated according to the Langmuir and Freundlich equations

Figure 2 shows adsorption isotherms calculated according to the Langmuir and Freundlich equations and experimental points. It can be seen from the obtained data that the Langmuir isotherm poorly describes the adsorption process. This is due to the fact that the Langmuir equation assumes single-layer homogeneous adsorption with a limited number of equivalent adsorption centers, where each center has a constant enthalpy and sorption activation energy. The Freundlich isotherm describes the adsorption process well in the region of high concentrations, but is completely inapplicable in the region of low concentrations, for which it has been criticized several times.

The most accurately studied adsorption process is described by the Redlich-Peterson and Toth models (fig. 3), as evidenced by the lowest values of χ^2. This indicates the predominantly chemical nature of adsorption and that the adsorption centers are not identical in their properties. The Redlich-Peterson isotherm (fig. 3*a*) was developed as a hybrid model of the Langmuir and Freundlich isotherms. The Toth isotherm (fig. 3*b*) was developed to improve the approximation of the experimental data by the Langmuir isotherm. It is useful for describing heterogeneous adsorption systems and satisfactorily describes equilibria at both low and high concentrations of the adsorbent. The form of the model equation assumes an asymmetric quasi-Gaussian energy distribution, with most adsorption centers having an adsorption energy below the average value. The results obtained show that clays of the Maykop series of a low degree of conversion actively adsorb mercury from aqueous solutions. The maximum adsorption is more than 10 mg/g (1 wt.%), which suggests that a significant amount of mercury can accumulate in these clays.

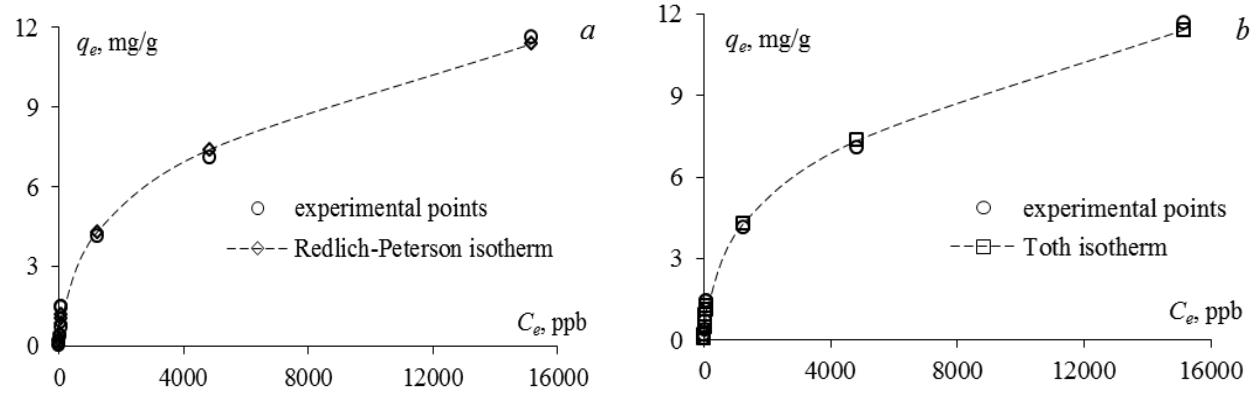

Fig. 3. Isotherms of mercury adsorption on clay of the Maykop series calculated according to the equations of Redlich-Peterson (*a*) and Toth (*b*)

Thus, it was found that when the mass ratio of the sorbent and the solution is 1: 500, the adsorption equilibrium occurs after 4 days with active shaking and after 2 weeks without shaking. At this point, the completeness of removal reaches 96% and 94%, respectively. With a longer exposure (1 month), equilibrium is maintained. The experimental data on mercury adsorption are best described by the Redlich-Peterson and Toth equations.

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References

Ivanov V.V. Ecological geochemistry of elements. Ref. book, in 6 books. Book 5. M.: Nedra, 1996. – 352 p.

Salavatova D.S., Fiaizullina R.V. Modeling of Mercury (II) Adsorption on Clays of the Maykop Series // Proceedings of the X All-Russian School of Young Scientists Experimental Mineralogy, Petrology and Geochemistry. IEM RAS Chernogolovka, 2019. – P. 122-124.

Fiaizullina R.V., Kuznetsov E.V., Salavatova D.S. Adsorption of Mercury from an Aqueous Solution on a Synthetic Organosilicon Sorbent // Mos. Univ. Geol. Bull., 2020. Series 4: Geology. In Print.

Boulinguiez B., Le Cloirec P., Wolbert D. Revisiting the determination of Langmuir parameters application to tetrahydrothiophene adsorption onto activated carbon // Langmuir, 2008. Vol. 24. P. 6420-6424.

Freundlich H.M.F. Over the adsorption in solution // J. Phys. Chem., 1906. Vol. 57. P 385–470.

Langmuir I. The constitution and fundamental properties of solids and liquids // J. Am. Chem. Soc., 1916. Vol. 38(11). P. 2221-2295.

Mieiro C.L., Pato P., Pereira E., Mirante F., Coutinho J.A.P., Pinheiro L.M., Magalhães V.H., Duarte A.C. Total mercury in sediments from mud volcanoes in Gulf of Cadiz // Marine Pollution Bulletin, 2007. Vol. 54. P. 1539-1544.

Redlich O., Peterson D.L. A useful adsorption isotherm // J. Phys. Chem., 1959. Vol. 63. P. 1024-1026.

Toth J. State equations of the solid gas interface layer // Acta Chem. Acad. Hung., 1971. Vol. 69. P. 311-317.