Salavatova D. S., Bychkov D. A., Fiaizullina R.V. **The Maikop series clays and mud volcano clays adsorption properties on mercury (ii) ions** *UDC 550.4.02 550.41 550.424*

Lomonosov Moscow State University, Faculty of Geology, Department of Geochemistry, Russia, Moscow
(*salavatova-jamilya2012@yandex.ru*, *krok@geol.msu.ru*, *fiaizullina@geol.msu.ru*)

Abstract. The acid-base properties of the surface of the Maikop series clays and mud volcano clays, as well as their adsorption properties with respect to mercury (II) ions, were studied. It is shown that when the mass ratio of the sorbent and solution is 1:900, adsorption equilibrium occurs after 4 days with active stirring. Experimental data on mercury adsorption from chloride-bicarbonate solution on natural sorbents are best described by the Redlich-Peterson and Toth equations. The process of mercury adsorption on clays of the Maikop series is more intense than on mud volcano clays.

Keywords: *adsorption, mercury, Maikop series, mud volcanoes, adsorption kinetics, adsorption isotherms.*

The behavior of mercury in the mud volcanic process has not been sufficiently studied. There is an opinion that the Maikop series clays absorb mercury, then sink into the zone of the mud volcanic chamber and are transformed, resulting in the release of mercury, which then begins its own behavior in the mud volcanic system. The main route of mercury migration to the surface is supposed to be transport in the gas phase, mainly methane. The study of the adsorption properties of Maikop series clays and mud volcano clays with respect to mercury ions can be one of the ways to test this assumption. In addition, information about the adsorption properties of a particular sorbent can help in making a decision on its use as an adsorbent for cleaning the environment from mercury pollution (Fiaizullina et al., 2017; Fiaizullina et al., 2020).

The natural material was provided by A.Yu. Bychkov, professor of the Geological Faculty of Lomonosov Moscow State University. and represents Maikop series clays and mud volcano clays. Both samples were taken in the Crimea in 2018: the first one was taken near the village of Zubakino in the riverbed Alma, where the outcrop is a homogeneous greenish-gray clays with a rare foraminiferal fauna. The second is on the Bulganak field on the slope of the Andrusov hill. The concentrations of mercury (II) ions were determined by the atomic absorption method with Zeeman correction of nonselective absorption on a RA-915M spectrometer with a flameless type of atomization (Lumex, Russia). The integration of the analytical signal and the calculation of the mercury concentration were carried out using the RAPID software. To implement the "cold vapor" method, the attachment RP-92 (Lumex, Russia) was used. Mercury cations were reduced with a 10% solution of tin (II) chloride of 2-aqueous in 15% sulfuric acid.

The concentration of adsorbed mercury was determined by the difference in concentrations in solutions according to the equation:

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

where q_e is adsorption capacity (ppm); 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). As the pH electrode, the EGK-10601 combined glass electrode (Measuring equipment, Moscow) was used. The solutions were mixed with an Orbital Shaker OS-20 (BioSan, Latvia).

Kinetics of mercury adsorption. An experimental study of the kinetics of mercury adsorption on clays included 2 series: the first was manually mixed 3 times a day, the second was continuously mixed on a BioSan OS-20 shaker at a speed of 140 rpm. The result of studying the kinetics of mercury adsorption on natural material is shown in Figure 1. The graph shows that adsorption is more active on both sorbents in the presence of continuous mixing.

When conducting experiments under static conditions, it should be taken into account that, in addition to the sorption process, there is also a loss of mercury over time. Therefore, the chosen exposure time for an isothermal experiment should be sufficient to carry out almost complete sorption of mercury with its insignificant losses. First of all, experiments were carried out without using a shaker, according to the results of which it was shown that the time to establish equilibrium is much longer than allowed from the point of view of mercury losses. Then, in an experiment with continuous stirring, it was possible to choose an exposure time that meets the above requirements and is 4 days. Losses were taken into account by measuring the mercury content at different time intervals in a sample with the same mercury concentration as in the samples of the kinetic series, but in the absence of solid matter.

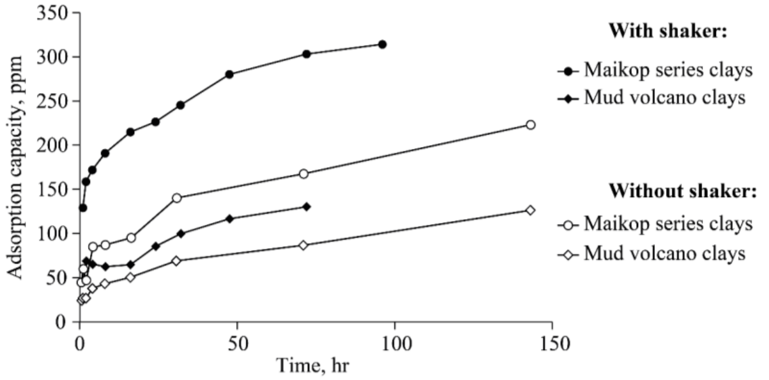

Fig. 1. Adsorption capacity of mercury on clays depending on time

Mercury adsorption isotherms. An analysis of adsorption isotherms gives an idea of the features of the adsorption process, the efficiency of the selected sorbent, and makes it possible to evaluate the possibility of its use for the absorption of certain substances. In this paper, the analysis of isotherms was carried out using the equations of Langmuir, Freundlich, Redlich-Peterson and Toth. The parameters of these equations were determined by minimizing the nonlinear chi-square test χ^2 using the "search for solution" add-in in Microsoft Excel. The χ^2 was calculated according to the formula:

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

where χ^2 is nonlinear chi-square test, $q_e^{\mathrm{calc.}}$ is calculated adsorption capacity (ppm), $q_e^{\mathrm{meas.}}$ is measured adsorption capacity (ppm). The values of the parameters of the equations and the χ^2 are given in table 1.

Adsorption isotherms calculated using the Langmuir, Freundlich, Redlich-Peterson and Toth equations and experimental points are shown in Figure 2 for Maikop series clays and Figure 3 for mud volcano clays. According to the data obtained, it can be seen that the adsorption of mercury on both sorbents is best described by the Redlich-Petrson equation. However, the Redlich-Peterson model is derived only on the basis of mathematical considerations and is based on them. Therefore, it was decided to consider another model, the Toth isotherm, which, in turn, describes the adsorption process just as well. The form of Toth's equation assumes an asymmetric quasi-Gaussian energy distribution, with most adsorption sites having adsorption energies below the mean value. Summarizing the above, the experimental data on mercury adsorption on natural sorbents are best described by the Redlich-Peterson and Toth equations, which indicates the predominantly chemical nature of adsorption and that the adsorption sites are not identical in their properties.

Table 1. Parameters of Hg^{2+} adsorption isotherms on clays calculated using four models and χ^2

Isotherm	**Parameter**	**Value**		χ^2	
		Maikop series clays	**Mud volcano clays**	**Maikop series clays**	**Mud volcano clays**
Langmuir	$q\infty$, ppm	421	142	1.6	1.2
	K_L, g/μg	5.72	6.05		
Freundlich	n	2.30	2.57	9.8	2.0
	K_F	20.9	9.76		
Redlich-Peterson	a_R	$7.15 \cdot 10^{-4}$	$8.16 \cdot 10^{-5}$	0.3	0.8
	g	1.28	1.60		
	K_R	1.90	0.553		
Toth	a_T	457	663	0.4	0.9
	t	0.615	0.468		
	K_T	44300	737000		

Figures 1, 2, and 3 show that process of mercury adsorption on Maikop series clays occurs more intensively than on mud volcano clays. This may be due to their mineral composition – in the Maikop series clays, among the clay minerals, the group of smectites predominates, their content is 2.4 times greater than the content of illites, and in the mud volcano clays, the amount of smectites and illites is the same. As is known, smectites have a mobile crystal lattice, as a result of which they are prone to swelling. The crystal lattice of illites is rigid; therefore, swelling is not typical for this group of minerals (Sokolov, 2000). Thus, Maikop series clays are subject to swelling to a greater extent than mud volcano clays; therefore, this may explain the fact that mercury adsorption on them is more intense.

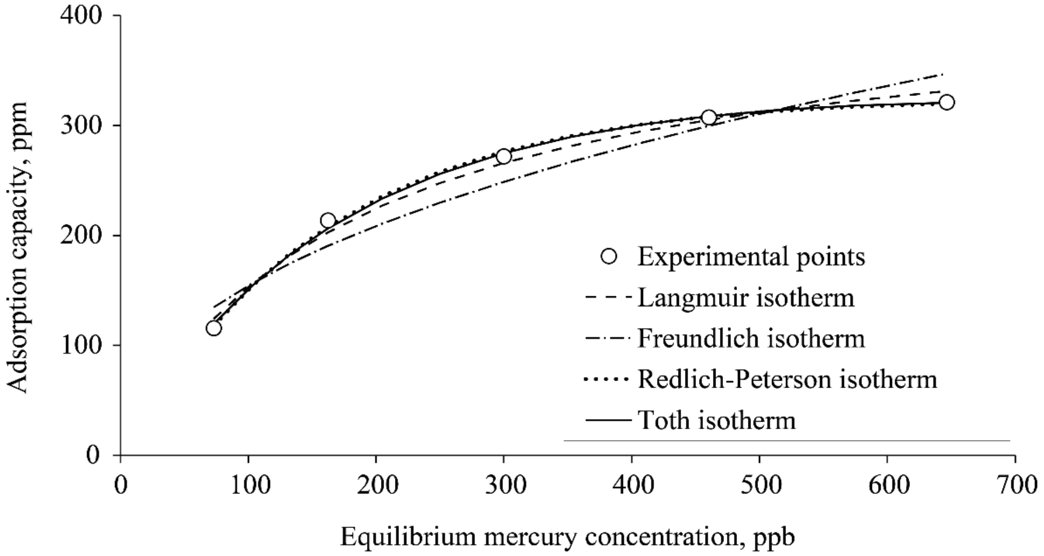

Fig. 2. Adsorption isotherms calculated using the Langmuir, Freundlich, Redlich-Peterson and Toth equations and experimental points for the Maikop series clays

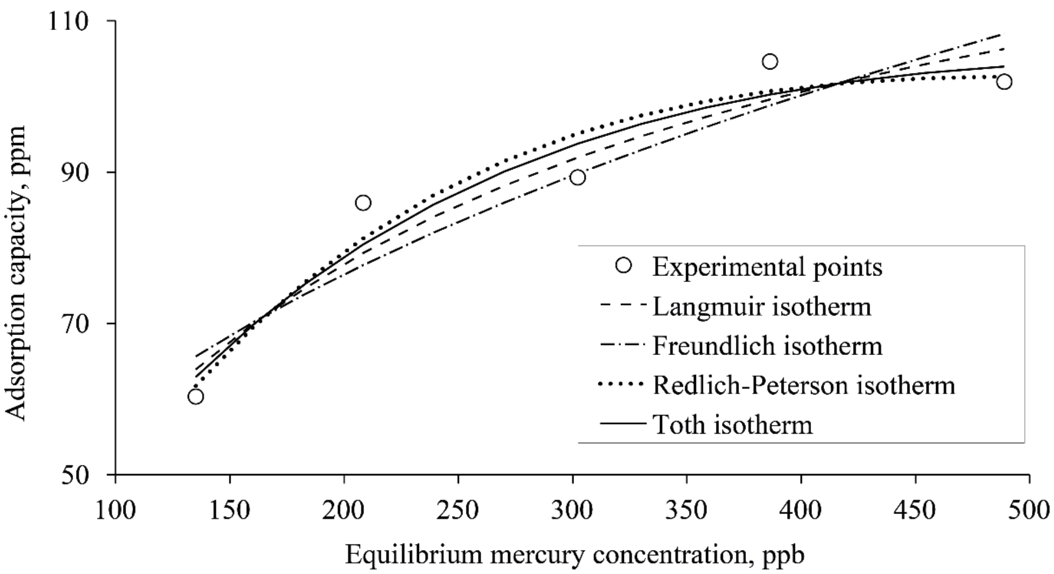

Fig. 3. Adsorption isotherms calculated using the Langmuir, Freundlich, Redlich-Peterson and Toth equations and experimental points for the mud volcano clays

The result of studying the adsorption properties of clays is consistent with the known data (for example, (Kholodov, 2002)) that the mud volcanic process is accompanied by the presence of an illite-smectite transition, when porous and plastic smectites are replaced by illites as a result of hydromica. The Maikop series clays, which contain a large amount of smectites, adsorb mercury, then sink into the zone of the mud volcanic chamber and transform, resulting in the transition of smectite to illite and the release of mercury, which then begins its own behavior in the mud volcanic system. It is assumed that mercury is removed mainly in the methane gas phase. In the work of Karasik M.A. and Morozov V.I. (Karasik, Morozov, 1966) it was shown that the content of mercury in the hill gases of the Kerch Peninsula reaches 2 μg/m^3, and in the gases of the Taman Peninsula it is up to 10 μg/m^3, and this is 1000 and 5000 times, respectively, more than the average concentration of mercury in the atmospheric air equal to 2 ng/m^3 (Granovsky et al., 2001).

References

Fiaizullina R. V., Kuznetsov E. V., Salavatova D. S. Mercury adsorption from aqueous solution using a synthetic organosilicon sorbent // Moscow University Geology Bulletin, 2020. Vol. 75(4). P. 381–386.

Fiaizullina R.V., Makarova M.A., Abrosimova N.A. The possibility of wastewater treatment of heavy metals by natural sorbents // Proceedings of 17 international multidisciplinary scientific geoconference SGEM 2017. Vol. 52 of *Soils, Forest ecosystems*. STEF92 Sofia, Bulgaria, 2017. P. 1027–1034.

Granovsky E.I., Khasenova S.K., Darisheva A.M., Frolova V.A. Mercury pollution of the environment and methods of demercurization. Analytical review. Almaty: KazgosINTI, 2001. – 98 p. In Rus. (*Грановский Э.И., Хасенова С.К., Даришева А.М., Фролова В.А.* Загрязнение ртутью окружающей среды и методы демеркуризации. Аналитический обзор. Алматы: Изд-во КазгосИНТИ, 2001. – 98 с.)

Karasik M.A., Morozov V.I. Features of the distribution of mercury in the products of mud volcanism of the Kerch-Taman province // Geochemistry, 1966. No. 6. P. 668-677. In Rus. (*Карасик М.А., Морозов В.И.* Особенности распространения ртути в продуктах грязевого вулканизма Керченско-Таманской провинции // Геохимия, 1966. № 6. С. 668-677.)

Kholodov V.N. On the nature of mud volcanoes // Priroda, 2002. No. 11. P. 47–58. In Rus. (*Холодов В.Н.* О природе грязевых вулканов // Природа, 2002. № 11. С. 47–58.)

Sokolov V.N. Clay rocks and their properties // Soros Educational Journal, 2000. No. 9. P. 59-66. In Rus. (*Соколов В.Н.* Глинистые породы и их свойства // Соросовский образовательный журнал, 2000. № 9. С. 59-66.)