Salavatova D.S., Bychkov D.A., Fiaizullina R.V. Adsorption properties of sand-gel material in relation to mercury (ii) ions in the presence of other metals. *UDC 550.4.02 550.41 550.42*

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Abstract. The adsorption properties of sand-gel material (SGM) with respect to mercury (II) ions were studied. It has been shown that studying adsorption under static conditions is incorrect, since upon contact with the sorbent, oxalates pass into the solution, forming stable complexes with mercury that are not capable of sorption. The efficiency of mercury absorption by SGM in the presence of nickel, copper, zinc and lead was assessed. It has been experimentally shown that the adsorption value of mercury on SGM reaches 0.4 mg/g. Metal adsorption decreases in the order Hg > Pb > Cu > Zn > Ni. The absorption capacity of the sorbent for mercury (II) ions is 0.67 mg/cm^3. It has been established that the studied material effectively absorbs mercury (II) ions, and therefore can be used for wastewater treatment with mercury contamination.

Keywords: *adsorption; mercury; synthetic sorbents*

The problems of protecting the environment from various pollutants do not lose their relevance to this day. Mercury is one of the most toxic metals. Mercury-containing waste belongs to hazard class I in all environments. Improper handling of mercury and its compounds has led to several environmental tragedies, resulting in widespread illness and loss of life.

The problem of mercury pollution is quite acute in the city of Usolye-Sibirskoye. During the operation of the "Usolyekhimprom" plant, the total emissions of mercury exceeded 1,700 tons. Most of the waste mercury was accumulated under the buildings of the mercury electrolysis workshop and in the sludge storage tank of the enterprise. About 24 tons of mercury are concentrated in the surface (up to 25 cm) layer of soils at the "Usolyekhimprom" industrial site and adjacent territories; its discharges with wastewater exceeded 37 tons; in the bottom sediments of the Bratsk Reservoir there are 63 tons of technical mercury (Koval et al., 2004). Despite the fact that the mercury electrolysis workshop at the "Usolyekhimprom" enterprise was closed in 1998, the plant's effluents continue to influence the composition of water and bottom sediments of the river Angara and Bratsk Reservoir, since the drainage system and treatment facilities of the enterprise are contaminated with mercury (Alieva et al., 2011). To process the chemical substances accumulated at the "Usolyekhimprom" industrial site, in particular mercury, it is necessary to take measures to eliminate the damage caused to the environment. A huge number of works, including ours, are devoted to the creation of adequate natural and artificial geochemical barriers (Fiaizullina et al., 2020; Salavatova et al., 2023, etc.). However, the contaminated area is quite large, about 600 hectares, so the barrier must be permeable to avoid waterlogging of the area.

In the Laboratory of the Geological Environment Protection of the Geological Faculty of Lomonosov Moscow State University, a sorbent was developed, which is a sand-gel material (SGM) based on an oxalum-alumina silicate gel-forming solution. An increase in the permeability of SGM is achieved by its mechanical destruction after the transition of the oxalum-alumina silicate solution to a gel-like state (Sergeev et al., 2021). This material is suitable for cleaning areas on an industrial scale, because it is cheap, has high permeability and can be produced directly at the site of contamination.

The manufacturing scheme of the proposed sorbent includes two stages: initially, sand is placed in a mixture consisting of liquid glass, solutions of oxalic acid and aluminum sulfate. And then, after a few hours, the gel-like mass is mixed and brought to an air-dry state (Kuleshova, Danchenko, 2019).

This work is devoted to the study of the adsorption properties of SGM in relation to mercury (II) ions from a polyelement solution containing, in addition to mercury, copper, nickel, zinc and lead.

The concentrations of mercury (II) ions were determined by the atomic absorption method on a RA-915M spectrometer with a flameless atomization type (Lumex, Russia). To implement the "cold vapor" method, the RP-92 attachment (Lumex, Russia) was used. The content of copper, nickel, zinc and lead was determined by the ICP-MS method on a Thermo Element-2 device (analyst, researcher at the Department of Geochemistry, Faculty of Geology, Lomonosov Moscow State University Nikolaeva I.Yu.).

The sorption of mercury on SGM was determined in two ways – in static and dynamic modes. To study the kinetics of mercury adsorption under static conditions, two series of experiments were carried out. In the first, the sorbent weight was 0.2 g, and the exposure time was from 1 to 24 hours. In the second series, the mass of the SGM was 0.6 g; exposure time – from 15 minutes to 4 days. In both series, the concentration of mercury (II) in each sample was 500 ppb, the volume of solutions was brought to 50 ml

with double-distilled water. The tubes were mixed manually 4 times a day.

It turned out that in a series with a larger mass of sorbent, a lower adsorption value is observed compared to a smaller mass of SGM, which is paradoxical. Based on this, two assumptions were made that: a) there is a dependence of sorption on the ratio of solid and liquid substances; b) there is a dependence on the test tubes, since 2 series of the experiment were carried out in test tubes from different manufacturers. For testing, an experiment was carried out with two parallel series in test tubes from Ningbo Greetmed and Jet Biofil (China) with different ratios of solid and liquid substances. The weight of the sample varied from 0.1 to 1 g, the initial concentration of mercury was 500 ppb, and the exposure time was 18 hours.

Based on the results of comparing the obtained data as sets with pairwise related measurements, it turned out that the deviation of the adsorption values in parallel series is not significant (Table 1). However, there is a clear dependence of sorption on the ratio of solid and liquid substances. This is due to the fact that upon contact with SGM, oxalates (oxalic acid salts) pass into solution, which form stable complexes with mercury – the stability constant of Hg(II)-oxalate is 4.6×10^9 (Pehkonen, Lin, 1998), therefore, studying the adsorption of mercury on this material under static conditions is incorrect. Due to the complex behavior of the sorbent, it was decided to determine the mercury absorption capacity of this sorbent under dynamic conditions. In this case, at the initial stage of pumping, the oxalates will be completely washed out and complexation will not affect the further sorption of mercury.

Table 1. The result of experiments with different ratios of SGM and solution volume (S – tubes manufactured by Ningbo Greetmed; Z – Jet Biofil tubes)

Sample	SGM mass, g	Initial mercury concentrations, ppb	Equilibrium mercury concentrations, ppb	Adsorption capacity of mercury, μg/g	Exposure time, hour
S-0,1g	0.101	521	436	42.1	18.0
S-0,3g	0.301	521	422	16.4	18.1
S-1g	1.002	521	447	3.70	18.3
Z-0,1g	0.100	521	423	48.9	18.5
Z-0,3g	0.298	519	413	17.9	18.6
Z-1g	0.997	520	434	4.34	19.0

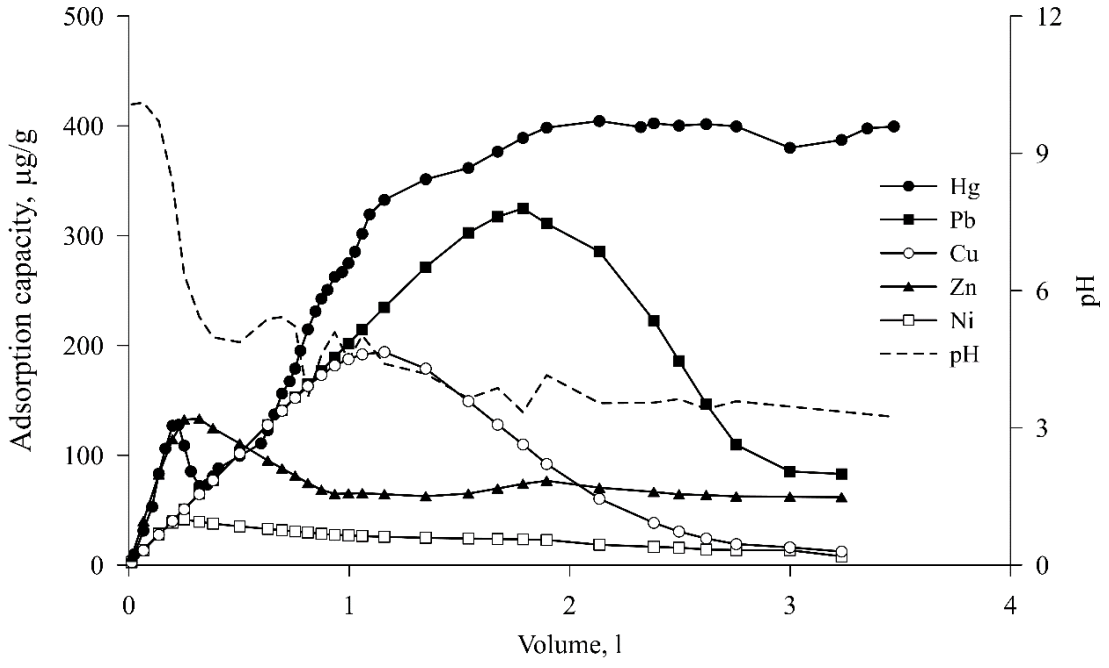

Fig. 1. Dependence of the value of metal adsorption on the volume of solution pumped through the SGM and the pH change curve

In a dynamic experiment, a solution containing copper, nickel, zinc, lead and mercury ions was pumped through a column packed with sorbent using a peristaltic pump with adjustable speed Masterflex C/L. The mass of the SGM was 47 g, its height was 4 cm, and the cross-sectional area of the column was 7.07 cm^2. The average pumping rate was 120 ml/day. The initial concentration of mercury, copper, nickel and lead in the solution was 10 ppm, and zinc – 30 ppm. Sampling from the output tube for analysis was carried out 1-2 times a day. A total of 48 samples were taken during the experiment. The air temperature in the laboratory during the experiment was 26.8±4.2℃.

Based on the results of the experiment, the total adsorption value at each point for each element was calculated (Fig. 1). The graph shows that the sorption of metals decreases in the order Hg > Pb > Cu > Zn > Ni. It should be noted that at the moment of a significant change in pH values from the alkaline region to the acidic region, a slight desorption of mercury is observed. At all other stages of pumping, mercury is adsorbed, reaching 0.4 mg/g in the limit. Considering that the mass of the SGM in the column is 47 g, the amount of mercury absorbed by the sorbent was 18.8 mg. Knowing the volume of the sorbent in the column (28.3 cm^3), it is easy to calculate the absorption capacity of the SGM for mercury (II) ions, which was 0.67 mg/cm^3.

Thus, the studies conducted confirm the effectiveness of SGM against mercury. The sorbent can be used as a horizontal and vertical geochemical barrier for the purification of liquid industrial waste from mercury, including in the presence of copper, zinc, nickel and lead.

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