Experimental geoecology

Fiaizullina R.V., Kuznetsov E.V., Salavatova D.S. Sorption properties of synthetic silicon organic sorbent PSTU-3F on mercury

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Abstract. The possibility of using synthetic silicone sorbent PSTU-3F for the adsorption removal of mercury from an aqueous solution has been studied. The dependence of mercury adsorption on the pH of the solution, the amount of the adsorbent and the duration of the contact of the solution with the adsorbent was investigated. It was shown that the amount of adsorption is the higher, the higher the acidity of the solution. This is due to the absolute dominance of the cationic form of the bivalent mercury Hg^{2+} and the negative charge of the surface of the sorbent. It has been established that an increase in the mass of the sorbent has a significant effect on the shift of the pH of the solutions to a more alkaline region. Therefore, the optimal ratio of the sorbent - solution should be considered the ratio of 1:1000. To interpret the equilibrium mercury adsorption data, an experimental adsorption isotherm was constructed, which was analyzed using the Langmuir and Freundlich equations. As a result, it was shown that the Freundlich equation describes the adsorption process significantly better than the Langmuir equation.

Keywords: *mercury adsorption, synthetic silicon organic sorbent, adsorption isotherms, Langmuir equation, Freundlich equation.*

Mercury and its compounds are an integral part of the environment, where they are usually found in extremely low concentrations. Analytical chemistry of mercury has visibly made a step forward over the last fifty years. However, there still exist natural reservoirs in which concentrations cannot be directly determined. In such cases, one solution is to use various kinds of synthetic sorbents that significantly lower the detection limit for mercury. An additional advantage of their use is the possibility of transporting accumulated mercury on the sorbent from the sampling site directly to the measurement site, i.e. in an equipped analytical laboratory. In areas with increased anthropogenic load, another problem is particularly acute, associated with elevated concentrations of this element. A large amount of data on the negative effects of mercury on the environment, including ours (Fiaizullina et al., 2017), indicates the need for industrial and wastewater treatment. In the absence of control and reliable protective devices, it enters the soil, surface and groundwater, and bottom sediments, having an extremely negative impact on the environment. In particular, entering the aquatic ecosystem, mercury accumulates and transforms in each subsequent link in the food chain, reaching the maximum content at its top. Analysis of currently existing methods of purification of natural and waste water from heavy metals showed that one of the most promising is the sorption method. The synthetic sorbent PSTU-3F, synthesized by a group of scientists from the A.E. Favorsky Irkutsk Institute of Chemistry SB RAS under the leadership of academician M.G. Voronkov, fits the role of a sorbent capable of providing a solution to these two diametrically opposite problems. The sorbent is a spatially cross-linked organosilicon polymer with thiocarbamide groups - poly [N, N '- bis (3-silesquioxanylpropyl) thiocarbamide] (PSTU-3), which is obtained by hydrolytic polycondensation in an aqueous medium at 90-100 °C N, N'-bis- (3-Triethoxysilylpropyl) thiocarbamide (Voronkov et al., 1991):

$$n\,[(C_2H_5O)_3SiCH_2CH_2CH_2NH]_2C{=}S + 6n\,H_2O \xrightarrow[-6n\,C_2H_5OH]{} \rightarrow(O_{1,5}SiCH_2CH_2CH_2NHC(S)NHCH_2CH_2CH_2SiO_{1,5})\,n$$

Its distinctive feature is increased thermal and chemical stability, which allows operation in aggressive environments. High chemical stability allows this sorbent to function in a wide range of acidity of the medium: from pH 12 to strong concentrated acids (Vasilyeva et al., 2010). Thus, the purpose of our work was to study the sorption properties of the PSTU-3F silicone sorbent on mercury. A number of factors can influence the course of adsorption: the amount of the adsorbent, the time of its contact with the solution, the temperature and the pH value. The laboratory air temperature throughout all experiments was 24.0±1.5 °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% solution of sodium borohydride in a 1% solution of sodium alkali. To control the acidity of the solutions, the pH meter Expert-001 (Econix-Expert, Moscow) was used. A combined glass electrode "EGC-10601" (Measuring equipment, Moscow) was used as a pH electrode. The concentration of adsorbed mercury was determined by the difference of concentrations in solutions by the equation:

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

where q_e is the amount of Hg(II) adsorbed at equilibrium is (mcg/g); C and C_e are the initial and equilibrium concentrations of metal ions in the solution respectively (ppm); m_{sol} is the mass of the solution (g); m_{sorb} is the mass of adsorbent (g).

Effect of pH. The acidity of the solution is one of the most important parameters controlling the absorption of heavy metals. In the case of PSTU-3F, we have shown that the process of mercury adsorption is most significant in the region of more acidic pH values (Fig. 1).

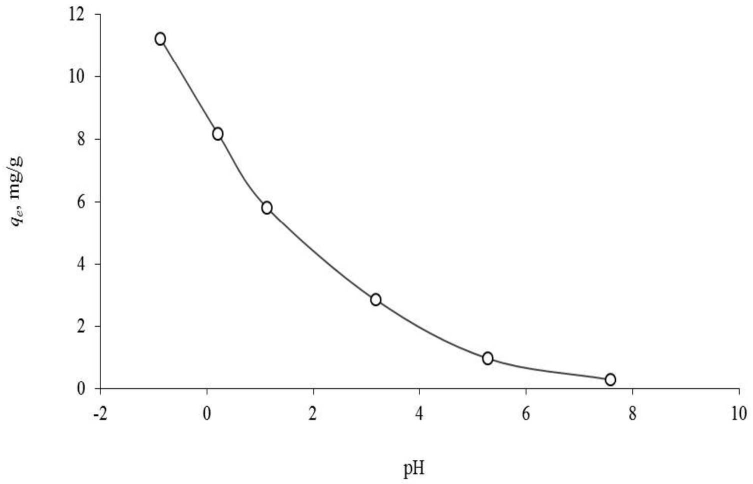

Fig. 1. Effect of pH on mercury (II) adsorption

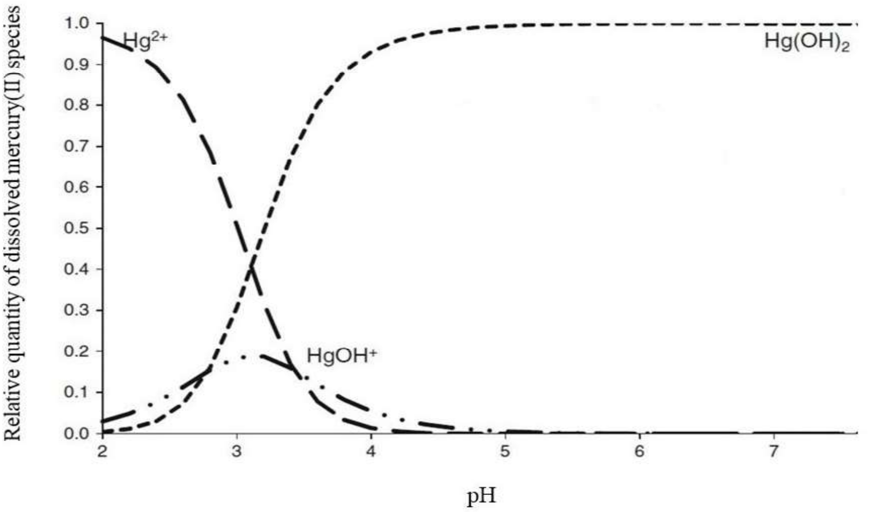

Fig. 2. The relative quantity of mercury (II) species (Nazarenko et al., 1979)

This is due to the dominance of the cationic form of mercury-divalent mercury Hg^{2+} in the area of strongly acidic solutions. This fact can be judged from the book (Nazarenko et al., 1979) on the hydrolysis of metal ions in highly diluted solutions (Fig. 2). It should also be noted that pH_{PZC} (points of zero charge) is probably in the near neutral medium, and the PSTU-3F sorbent, in the area under study, is a cation exchanger, i.e. negatively charged (Fig. 3).

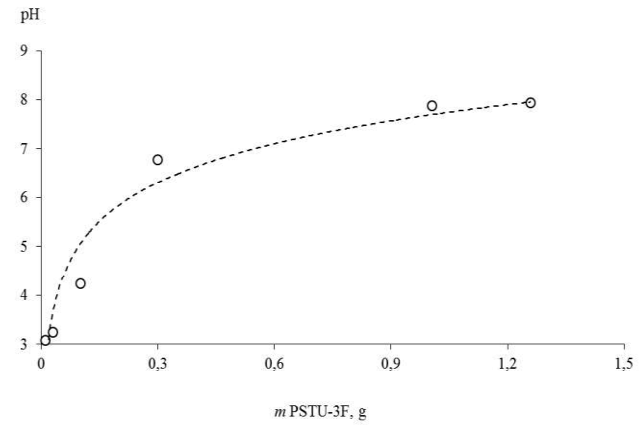

Fig. 3. The effect of the amount of sorbent on the pH of the solution

Therefore, Hg^{2+} cations are involved in the formation of the electric double layer, occupying the absolute majority of adsorption centers as a result of competing adsorption. The decrease in the amount of adsorbed substance, when shifted to the near-neutral and weakly alkaline zones, is associated with a decrease in the concentration of the Hg^{2+} particle, and in the region around the pH value equal to 3, the isoelectric point is located, in which the dominant form changes: the concentration of mercury (II) $Hg(OH)_2^0$ increases, having no charge, and, therefore, not able to be sorbed on the negatively charged surface of the sorbent. From Figure 3 the following fact also becomes obvious: with an increase in the amount of sorbent in solution, the acidity of the latter shifts to a more alkaline region. This can be explained by the formation of a double electric layer from the negatively charged surface of the sorbent, and positively charged protons attracted to it. It is obvious that with an increase in the amount of sorbent in the solution, the adsorption also increases, due to an increase in the sorbing surface. Consequently, due to the increase in the content of OH^- groups in the solution, the pH shifts to the alkaline region.

Adsorption kinetics. It should be noted that all the adsorption experiments described in this work were carried out under static conditions (without using shakers, i.e. without active mixing). Samples were mixed by hand for 2 minutes once a day. Under such conditions, equilibrium was achieved in less than a day, and the degree of mercury recovery from solutions in this case was more than 95%.

Adsorption isotherms. Analysis of adsorption isotherms allows you to set the features of the process, to assess the feasibility of the practical use of the sorbent to absorb any substances. In this work, isotherm analysis was performed using well-known equations: Langmuir and Freundlich. As a result, an experimental adsorption isotherm was constructed, as well as isotherms recalculated using the above equations (Fig. 4). The parameters of adsorption isotherms calculated by the Langmuir and Freundlich models are listed in Table 1.

Table 1. The parameters of adsorption isotherms calculated by two different models

Isotherm	Constants	Values	R^2
Langmuir	q_m, mg/g	5.57	0.9817
	K_L	0.0082	
Freundlich	n	1.508	0.9932
	K_F	0.1025	

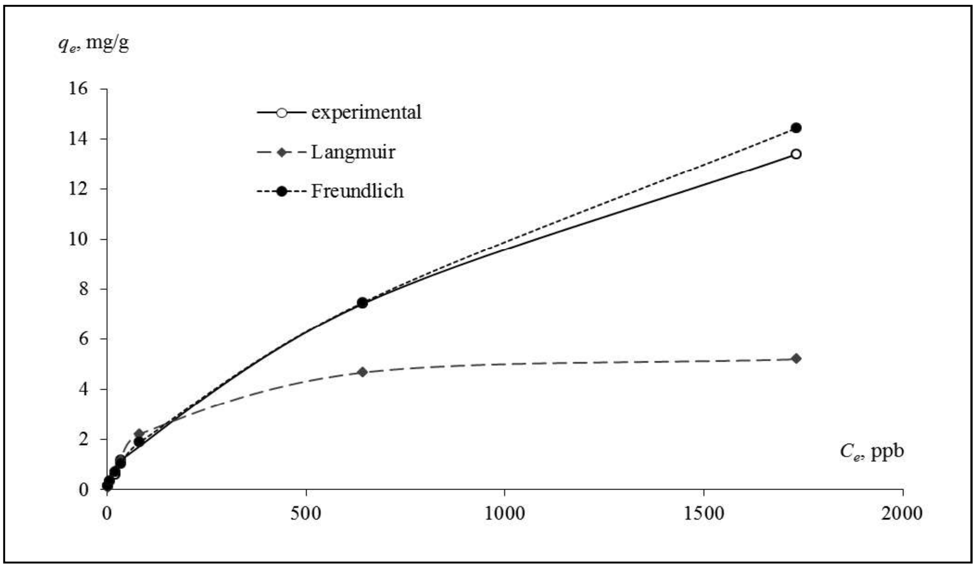

Fig. 4. Isotherms of mercury adsorption on PSTU-3F sorbent

From the data obtained, it becomes obvious that the most accurately studied adsorption process describes the Freundlich equation, as indicated by the value of R^2, greater than 0.99. From Figure 4 it becomes clear that the value of the limiting adsorption (q_m) was not achieved during the experiment, and its value significantly exceeds 15 mg/g, which indicates an impressive sorption capacity of the sorbent under study. The maximum adsorption value obtained from the Langmuir equation, corresponding to 5.57 mg/g, does not correspond to reality - it is significantly underestimated, which indicates the inapplicability of the theory of monomolecular adsorption in the case with the sorbent chosen by us.

Thus, it was found that mercury adsorption on the PSTU-3F sorbent is the higher, the higher the acidity value, i.e. maximum sorption occurs in the strongly acidic pH range. This is due to the absolute dominance of the cationic form of the bivalent mercury Hg^{2+} and the negative charge of the surface of the sorbent. The increase in the mass of the sorbent has a significant effect on the shift of the pH of the solutions to a more alkaline region. The optimal ratio of the sorbent - solution should be considered the ratio of 1:1000. Freundlich's equation most accurately describes the process of mercury adsorption on the silicone sorbent PSTU-3F.

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