

## **SYNTHESIS AND SORPTION PROPERTIES OF HYBRID ORGANO-SILICA MATERIALS IN RELATION TO HEAVY METALS**

*Yukhno G.D., Khristenko I.V., Efimova N.V., Krasnopyorova A.P.*

V.N. Karazin National University, Kharkiv, Ukraine

*alla.p.krasnopyorova@karazin.ua*

The problem of purification of natural and technical waters of heavy metals has important role for improvement of ecological situation in the areas of high technogenic activity for a human. For solution of this problem various sorption materials are widely used: natural and synthetic ion exchangers, organic-mineral materials, composites and others [1-3].

During the creation of new hybrid materials of different morphology with predictable properties, the sol-gel technology is used [4, 5]. By regulating the composition of organic and non-organic parts, the nature of modifier, the conditions of synthesis is created by the materials with different structural parameters and chemical properties, which find the application as sorbents, catalysts, carriers, etc. [6].

Throughout the research the organo-silica materials were obtained: the material 1 (KS+C45) and the material 2 (KS) and some of their characteristics and sorption properties in relation to heavy metals are researched.

Hybrid organo-silica materials were obtained by the sol-gel method in the presence of a gelation catalyst [7]. The volume ratio of tetraethoxysilane, ethyl spirit, and aqueous solution in the initial reaction mixture was 1: 2.5: 1. The concentration of the catalyst (ammonium hexafluoro silicate) was 0.02 mol/dm<sup>3</sup>.

For obtaining of the material 1 (KS+C45), an aqueous solution was used as a modifier 5,11,17,23 - tetrakis-diethylphosphonylmethyl-25,26,27,28-tetrapropoxycalix [4] arene (C45). The modifier was introduced into the polysiloxane framework of the matrix at the stage of hydrolytic polycondensation. The concentration of the modifier in the reaction mixture was 1.74 mmol/dm<sup>3</sup>.

During the obtaining of the material 2 (KS) the solution of the modifier into the reactionary mixture wasn't injected.

The specific surface area of the samples was estimated from the adsorption-desorption isotherms of nitrogen on the surface of materials ("Sorptometer Kelvin 1042", measurements were performed at the A.A. Chuiko Institute of Surface Chemistry, Senior Researcher of the Department of Chemisorption and Hybrid Materials, Dudarko O. A.) (Fig. 1). The specific surface area of the materials was calculated by the Brunauer-Emmett-Teller (BET) method, and the average pore diameter was found from the pore size distribution (the Barrett Table 1. Structural adsorption characteristics of materials-Joyner-Gelendi method) (Table 1).

The specific surface area of the samples was estimated from the adsorption-desorption isotherms of nitrogen on the surface of materials ("Sorptometer Kelvin 1042", measurements were performed at the A.A. Chuiko Institute of Surface Chemistry, Senior Researcher of the Department of Chemisorption and Hybrid Materials, Dudarko O. A.) (Fig. 1).

The specific surface area of the materials was calculated by the Brunauer-Emmett-Teller (BET) method, and the average pore diameter was found from the pore size distribution (the Barrett Table 1. Structural adsorption characteristics of materials-Joyner-Gelendi method) (Table 1).

The obtained isotherms of the nitrogen sorption (Fig.1), according to classification of IUPAC, can be referred to isotherms of the IVth type, which are characteristic of polymolecule adsorption on porous bodies, complicated by capillary condensation.

The type of hysteresis loop type, which is observed at the adsorption curve, according to classification [7], can be referred at H1, which is characteristic for which is typical for large-pore and medium-pore adsorbents, for globular and spongy structures.

Table 1. Structural adsorption characteristics of materials

material	$S_{уд}, M^2 \cdot g^{-1}$	$d_{пор}, nm$
1	347	9
2	340	8

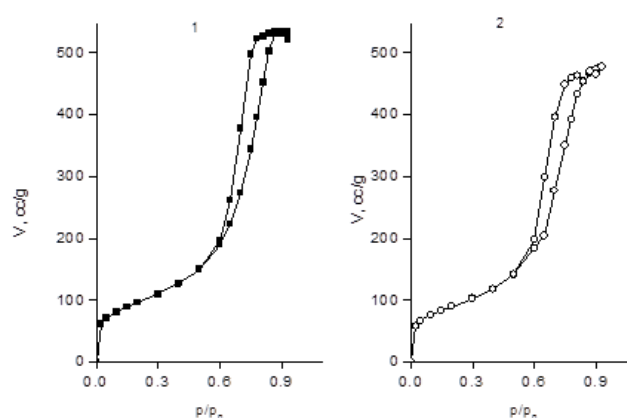


Figure 1 Nitrogen sorption-desorption isotherms on the surface of hybrid materials 1 (KS + C45) and 2 (KS).

The research of sorption of ions of  $H^+$ ,  $Cu^{2+}$  and  $Cd^{2+}$  at the surface of synthesized materials was conducted at the temperature of  $20 \pm 2^\circ C$ , ionic strength 0.1. Equilibrium ion concentrations in solution were determined by potentiometric method, using a laboratory ionomer I-160MI with glass electrode ESL 63-07, ion-selective electrodes ELIS-131Cu, ELIS-131Cd and silver chloride reference electrode (EVL 1-MZ). During the research of ions sorption of metals, the acidity of the suspensions under study was  $pH \sim 5.5 - 6$ .

Isotherm of sorption of ions  $H^+$  was described by equation of Lengmure, the adsorption capacity for the material 1 was 0.23 mmol/g and 0.14 mmol/g for material 2. The acidity of the environment in the near-surface layer of hybrid materials is related with the presence of surface silanol groups. Therefore, acidic-basic properties of the near-surface layer are conditioned by the properties of the matrix itself.

On the basis of the data about general and equilibrium concentrations of ions of metals in solution over the sorbent, the sorption concentration was calculated, isotherms of sorption were constructed (typical curved are given at Figures 4-5). The results of sorption of ions metals ( $Cu^{2+}$  и  $Cd^{2+}$ ) on the surface of the hybrid materials were described by equation of Freundlich (Fig. 4-5). Such correlation is a consequence of imperfect adsorption, which is accompanied by a cooperative effect and may indicate the formation of several types of complexes.

Close quantitative estimates of ions adsorption of adsorption of metal ions on the surface of hybrid materials claims about mixed mechanism of sorption, absorption of metal ions happens both by complexation and in the result of ions-exchange.

The extent of extraction of ions of metals was 72% ( $\text{Cu}^{2+}$ ) and 56% ( $\text{Cd}^{2+}$ ) by material 1 and 67% ( $\text{Cu}^{2+}$ ) and 51% ( $\text{Cd}^{2+}$ ) by material 2.

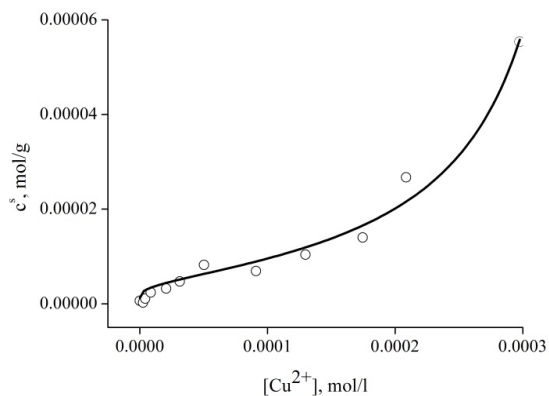


Figure 4. Isotherm of sorption of ions  $\text{Cu}^{2+}$  on the surface of the material 1

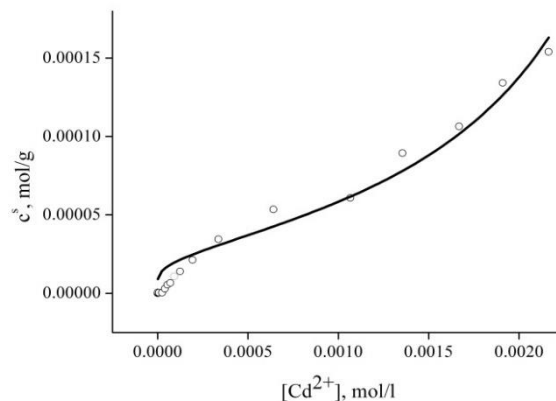


Figure 5. Isotherm of sorption of ions of  $\text{Cd}^{2+}$  on the surface of the material 2

#### Reference

1. Sorbtsiye ta ekstraktsiye vyluchennia radionuklidiv z ridkykh seredovyshch pryrodnyimi ta sintetychnymi materialami / A.P. Krasnopyorova, G.D. Yuhno, N.V. Efimova // Kompleksoutvorennia ta asotsiatsiya u rozchynach z uchastyu metalovmishchuyuchykh chastynok, funktsionalnykh I zabarvlenykh rehovyn: praktychni rishennia i napratsyuvannia: monografia / za redaktsiyeyu S.A. Shapovalova. — Kharkiv, 2018. — P. 65-105.
2. Tarasevich Yu.I., Shkutkova E.V., Yanush V. Sorbtsia ionov tiazhelykh metalov iz vodnykh rastvorov na hydroksiapatite. // *Chimia i technologia vody*. — 2012. — Vol. 34. — №3. — P. 213-225.
3. Efimova N.V., Krasnopyorova A.P., Yuhno G.D., Scheglovskaya A.A. Sorption of heavy metals by natural biopolymers // *Adsorption Science & Technology*. — 2017. — Vol. 35, No 7-8. — P. 595-601.
4. Sarı Yılmaz, M. Dere Özdemir, Ö. Pişkin Synthesis and characterization of MCM-41 with different methods and adsorption of  $\text{Sr}^{2+}$  on MCM-41 // *Research on Chemical Intermediates*. — 2015. — V. 41. — P. 199-211.
5. Ciesielczyk F., Bartczak P., Jesionowski T. Removal of cadmium(II) and lead(II) ions from model aqueous solutions using sol-gel-derived inorganic oxide adsorbent // *Adsorption*. — 2016. — Vol. 22. — P.445-458.
6. Fetisova Yu., Dudarko O., Bauman M., Lobnik A., Sliesarenko V. Adsorption of lead(II), cadmium(II) and dysprosium(III) from aqueous solutions using mesoporous silica modified with phosphonic acid groups // *J. Sol-Gel Sci. Technol.* — 2018. — Vol. 88, N1. — P.66-76.
7. Sing K.S.W., Everett D.H., Haul R.A.W., Moscou L., Pierotti R.A., Rouquerol J., Siemieniewska T. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity // *Pure Appl. Chem.* — 1985. — Vol. 57. — P. 603-619.