

UDC 544.723 + 547.458

NEW NANOPOROUS β -CYCLODEXTRIN-CONTAINING SILICAS FOR SORPTION OF HEAVY METAL NITRATES

L.A. Belyakova*, O.M. Shvets, D.Yu. Lyashenko

*Chuiko Institute of Surface Chemistry of National Academy of Sciences of Ukraine
17 General Naumov Str., Kyiv, 03164, Ukraine*

Nanoporous β -cyclodextrin-containing silicas, which differ by functional substituents of the wide edge of attached cyclic oligosaccharide molecules, were synthesized. Formation of the supramolecular structures (supermolecules), which chemical composition depends on the nature of adsorbed cations and functional substituents in the β -cyclodextrins molecules attached to the surface of organosilicas, was proved. The interpretation of interaction peculiarities of mercury and cadmium nitrates with the synthesized β -cyclodextrin-containing silicas was given started from the theory of hard and soft acids and bases.

INTRODUCTION

Mercury, cadmium and their compounds belong to the dangerous substances with maximum admissible concentrations in drinking water of 0.0005 and 0.001 mg·L⁻¹ for Hg(II) and Cd(II), correspondingly [1]. Even negligible content of mercury compounds in the drinking water results in their accumulation in the human body and causes serious diseases of thyroid gland, nervous and cardiovascular systems, and chronic poisoning with cadmium salts leads to anaemia, bone softening, liver and kidney failure [2, 3].

The sorption technologies are the most widespread in extraction, concentration and utilization of heavy metals. Natural and artificial ion-exchange materials are widely used for these purposes [4–6]. Deeper water and aqueous solutions treatment as well as extraction of small amounts of Hg(II) and Cd(II) is achieved with complexing sorbents [7–9]. Significant increasing of their adsorption affinity could be expected by the directional design of functional groups with high specificity and selectivity on the surface of suitable matrices [8–10], and also of supramolecular structures acting by the principles of “host – guest” or “lock – key” [11–13].

Disperse silica species as starting matrices for synthesis of new adsorbents are used due to hydrolytic, chemical, thermal and radiation stability, nonswelling structure and high reactivity of active sites of their surface [8, 9, 14, 15].

This paper presents the results of a study of sorption of Hg(II) and Cd(II) on disperse silicas

chemically modified with β -cyclodextrins, which differ in chemical nature of side functional groups of the wide edge of cyclic oligosaccharide molecules.

EXPERIMENTAL

Nanoporous amorphous silica – silochrome C-120 (Table 1) was used as starting silica matrix. Synthesis of β -CD-containing organosilicas was carried out through multistep sequential liquid-phase modification of silochrome surface (Scheme) initially with aminopropyl groups, then with β -cyclodextrin groups. Br- β -cyclodextrin for the study was provided by Prof. S.V. Ryabov. The change of bromoacetyl groups of chemically attached β -CD for thiosemicarbazidoacetyl groups was realized under conditions of optimal running of surface reaction of nucleophilic substitution [16–18].

Parameters of the porous structure of starting and modified silicas were calculated from low-temperature nitrogen adsorption-desorption isotherms [19] measured by Sorptometer KELVIN 1042.

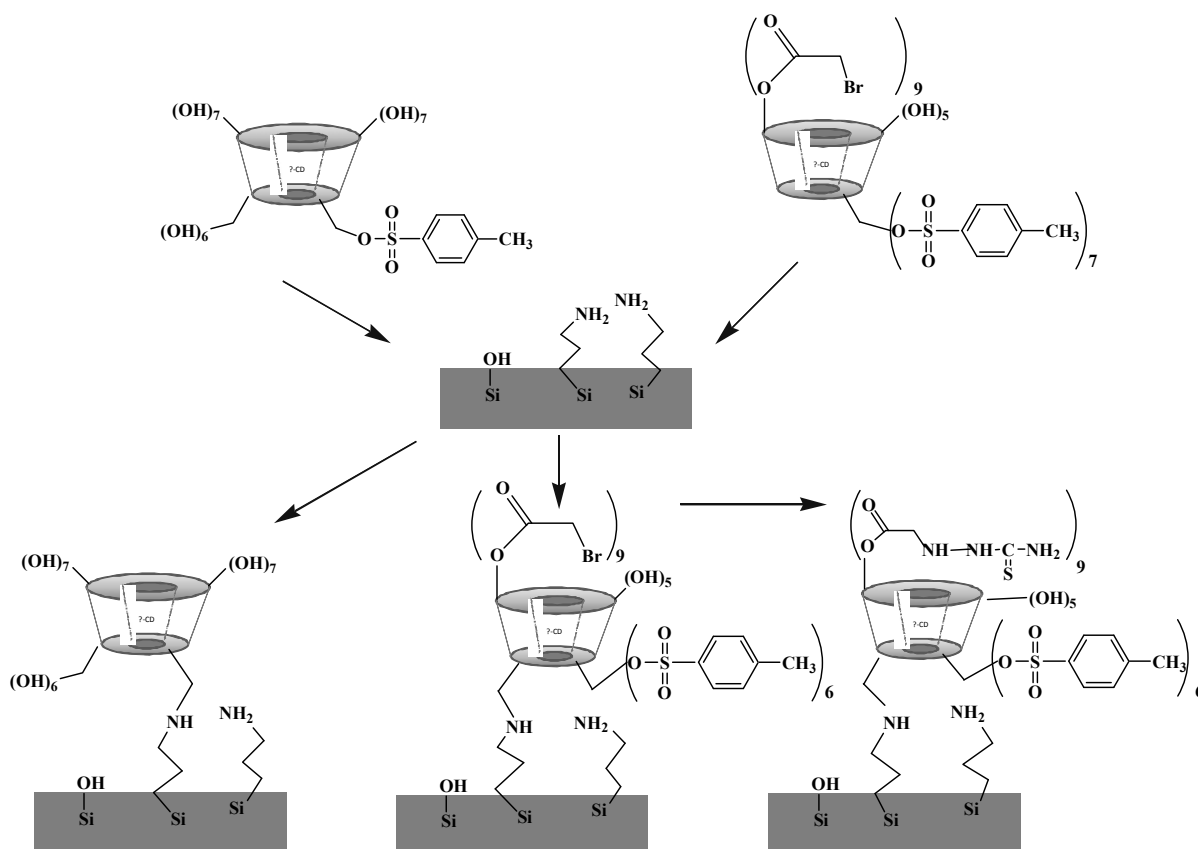
Chemical composition of the silicas surface was determined by potentiometric titration (Ionometer I-120.1) and elemental analysis (Elemental Analyzer EA 1110) [20].

Infrared transmission spectra of organosilicas were registered in the frequency range 4000–500 cm⁻¹ using a Thermo Nicolet NEXUS FT-IR spectrophotometer. The plates of ~ 30 mg each were compacted under a pressure of 10⁸ Pa for the recording IR spectra [20].

* corresponding author mila.belyakova@gmail.com
CPTS 2012. V. 3. N 4

Research of morphology of silica surfaces was carried out on JEOL JSM-6400 scanning

electron microscope (magnification $1 \cdot 10^3$ – $5 \cdot 10^4$, operating at 3–30 keV) [21].



Scheme. Synthesis of functional β -cyclodextrin-containing silicas

Sorption of mercury (II) and cadmium (II) cations by silicas depending on the time of contact and solution concentration was studied from the $2.5 \cdot 10^{-4}$ – $4.0 \cdot 10^{-3}$ mol·L⁻¹ aqueous solutions of corresponding nitrates with pH ~ 1 at 22 °C under static conditions by multibatch procedure. The amount of Hg(II) ions in the initial and equilibrium solutions was analyzed by atomic absorption spectrometry using a Pye Unicam SP-9 spectrometer and also by means of trilonometric back titration [22], Cd(II) – spectrophotometrically following the intensity of absorption band at $\lambda_{\max} = 576$ nm on a Perkin–Elmer Lambda 35 spectrophotometer using xylenol orange as a reagent [23].

The relative content of various forms of mercury (II) and cadmium (II) ions in a solution at pH 1–6 was calculated using Chemical Equilibria in Aquatic System Software (was written by Wilko Verweij, 1999–2006).

The results of equilibrium sorption of Hg(II) and Cd(II) have been analyzed by equations of Langmuir isotherm [24]:

$$C_{eq}/a_{eq} = 1/(K_L \cdot a_m) + (1/a_m) \cdot C_{eq},$$

where C_{eq} – the equilibrium concentration of adsorptive, mg·L⁻¹; a_{eq} – the equilibrium adsorption, mg·g⁻¹; K_L – Langmuir constant characterizing adsorption energy, L·mg⁻¹; a_m – the adsorption capacity of monolayer, mg·g⁻¹, and Freundlich isotherm [25]:

$$\lg a_{eq} = \lg K_F + (1/n) \cdot \lg C_{eq},$$

where a_{eq} – the equilibrium adsorption, mg·g⁻¹; K_F – Freundlich constant (adsorption capacity), mg·g⁻¹; $1/n$ – Freundlich constant characterizing adsorption intensity; C_{eq} – the equilibrium concentration of adsorptive, mg·L⁻¹.

The separation factor R_L [26] was calculated by the formula:

$$R_L = \frac{I}{(1 + K_L \cdot C_0)},$$

where C_0 – the initial concentration of the adsorptive, $\text{mg}\cdot\text{L}^{-1}$; K_L – Langmuir constant, $\text{L}\cdot\text{mg}^{-1}$.

Lagergren's kinetic models for the processes of the pseudo-first and the pseudo-second order were used for analysis of the kinetic curves of Hg(II) and Cd(II) sorption [26]. Integral form of Lagergren's kinetic model for pseudo-first order processes is expressed by the equation:

$$\ln(a_{eq} - a_t) = \ln a_{eq} - k_1 t,$$

where a_t and a_{eq} – the adsorption at time t and at the equilibrium state, $\text{mg}\cdot\text{g}^{-1}$; k_1 – the rate constant of adsorption, min^{-1} .

The equation of the pseudo-second order of Lagergren's kinetic model is given by:

$$\frac{t}{a_t} = \frac{1}{(k_2 \cdot a_{eq}^2)} + \frac{t}{a_{eq}},$$

where k_2 – the rate constant of adsorption, $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$.

RESULTS AND DISCUSSION

Chemical modification of surface of the starting silochrome with β -cyclodextrin and its functional derivatives causes regular decrease in the specific surface (by 26–32 %), sorption volume (by 25–48 %) and diameter (by 37–63 %) of pores. Nevertheless, β -CD-silicas

remain highly dispersive materials with nanosized pores (Table 1). Therefore, it can be supposed that the sorption of mercury (II) and cadmium (II) onto β -cyclodextrin-containing silicas will not be complicated by inner diffusion.

Indeed, sorption equilibrium on the β -cyclodextrin-containing silicas is reached in 15 min (Fig. 1). The rate constants of sorption of Hg(II) and Cd(II) have been calculated (Table 2) using Lagergren's equations [26]. Lagergren model for reactions of the pseudo-first order describes well the sorption processes in which the adsorbate interacts with the active sites of the adsorbent having the same chemical composition and structure. The model of the pseudo-second order is more complex and suggests the implementation of parallel or successive processes with various rates including adsorption on active sites of variable composition and structure.

The kinetic curve of mercury (II) sorption onto silica 3 is well fitted to linear form of Lagergren equation for the pseudo-first order processes, but in the case of cadmium (II) it corresponds to reaction of the pseudo-second order. The sorption of Hg(II) onto silicas 4 and 5 fits to the pseudo-second order processes model, whereas for Cd(II) it obeys Lagergren equation for the pseudo-first order reactions (Fig. 2).

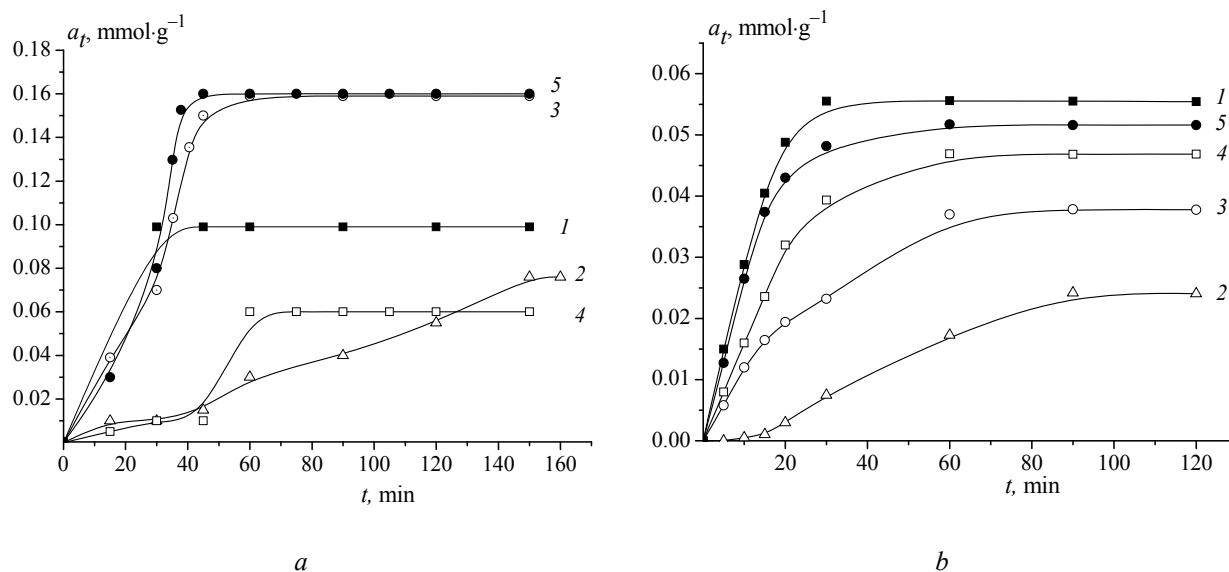


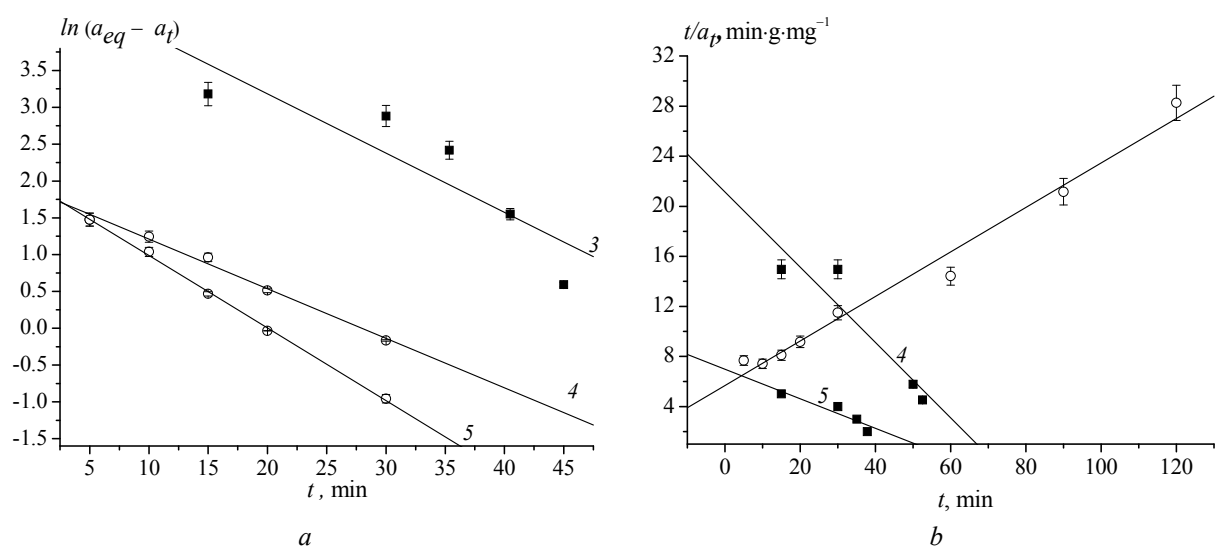
Fig. 1. Kinetic curves of mercury (II) (a) and cadmium (II) (b) sorption on organosilicas 1–5

Table 1. Chemical composition of surface layer and structural characteristics of synthesized silicas

Silica	Surface functional groups	Chemical elements content, %					Concentration of functional groups		Specific surface, $\text{m}^2\cdot\text{g}^{-1}$	Summary volume of pores, $\text{cm}^3\cdot\text{g}^{-1}$	Average diameter of pores, nm
		C	H	N	S	Br	$\text{mmol}\cdot\text{g}^{-1}$	$\mu\text{mol}\cdot\text{m}^{-2}$			
1	$\equiv\text{Si}-\text{OH}$	–	–	–	–	–	0.40	3.38	133	0.80	46
2	$\equiv\text{Si}-\text{OH}$						0.12	1.08	114	0.75	27
3	$\equiv\text{Si}-\text{O}-\text{Si}(\text{CH}_2)_3\text{NH}_2$	1.00	0.45	0.40	–	–	0.28	2.52	98	0.60	29
	$\equiv\text{Si}-\text{OH}$						0.12	1.22			
	$\equiv\text{Si}-\text{O}-\text{Si}(\text{CH}_2)_3\text{NH}_2$						0.24	2.44			
4	$\equiv\text{Si}-\text{O}-\text{Si}(\text{CH}_2)_3\text{NH}-\beta\text{-CD}$	2.80	0.70	0.40	–	–	0.035	0.36	95	0.50	24
	$\equiv\text{Si}-\text{OH}$						0.12	1.26			
	$\equiv\text{Si}-\text{O}-\text{Si}(\text{CH}_2)_3\text{NH}_2$						0.27	2.84			
5	$\equiv\text{Si}-\text{O}-\text{Si}(\text{CH}_2)_3\text{NH}-\beta\text{-CD}-(\text{CO}-\text{CH}_2\text{Br})_9$	2.20	0.60	0.40	0.20	0.70	0.01	0.11	90	0.42	17
	$\equiv\text{Si}-\text{OH}$						0.12	1.33			
	$\equiv\text{Si}-\text{O}-\text{Si}(\text{CH}_2)_3\text{NH}_2$						0.27	3.00			
5	$\equiv\text{Si}-\text{O}-\text{Si}(\text{CH}_2)_3\text{NH}-\beta\text{-CD}-(\text{CO}-\text{CH}_2-\text{NH}-\text{NH}-\text{CS}-\text{NH}_2)_9$	2.30	0.65	0.80	0.50	–	0.01	0.11			
	$\equiv\text{Si}-\text{OH}$										
	$\equiv\text{Si}-\text{O}-\text{Si}(\text{CH}_2)_3\text{NH}_2$										

Table 2. Kinetic parameters of mercury (II) and cadmium (II) sorption in coordinates of Lagergren model for processes of pseudo-first and pseudo-second orders

Silica	Hg(II)				Cd(II)			
	k_1, min^{-1}	R_1^2	$k_2, \text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$	R_2^2	k_1, min^{-1}	R_1^2	$k_2, \text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$	R_2^2
3	5.9 ± 0.3	0.92	0.055 ± 0.003	0.77	1.90 ± 0.1	0.96	0.312 ± 0.019	0.99
4	4.7 ± 0.2	0.70	0.02 ± 0.001	0.79	1.88 ± 0.1	0.99	0.233 ± 0.014	0.98
5	6.5 ± 0.3	0.87	0.016 ± 0.0008	0.98	1.97 ± 0.1	0.99	0.219 ± 0.013	0.96

**Fig. 2.** Kinetic curves of mercury (■) and cadmium (○) sorption on silicas 3–5 in coordinates of Lagergren equations for processes of pseudo-first (a) and pseudo-second (b) orders

The results of equilibrium sorption study are presented in Figure 3. The silicas 1 and 2 do not adsorb effectively cations of mercury (II) and cadmium (II) from $0.001 \text{ mol}\cdot\text{L}^{-1}$ aqueous solutions. The sorption only takes place provided their content increases by one order of magnitude [27, 28], and distribution coefficients do not exceed 10^1 (Table 3). The reason for the low sorption ability of silica 1 relative to Hg(II) and Cd(II) may be the lack of cation exchange at $\text{pH} = 1\text{--}3$, since silochrome refers to weakly acidic exchangers ($\text{p}K_a = 6.90$), and the portion of ionized silanol groups calculated using Henderson-Hasselbalch equation [29], within this pH range does not exceed 0.01%. Aminopropyl groups of silica 2 in acidic range are present, in the main, in protonated form [20] ($\text{p}K_b = 4.10$) and therefore do not participate in complex formation with Hg(II) and Cd(II).

The silicas modified with β -CD and its functional derivatives adsorb mercury (II) and cadmium (II) already at low concentrations of in a solution (Fig. 3); besides, Hg(II) adsorbs better than Cd(II). Sorption ability increases in both cases in the order: silica 3 < silica 4 < silica 5. Moreover, the sorption capacity of β -cyclodextrin-containing silicas exceeds the amount of chemically attached β -CD molecules in several times, and distribution coefficients rise by 2–3 orders of magnitude (Table 3). At the same time, the total concentrations of functional groups on the surface of silicas 1–5 (Scheme, Table 1) are identical, and only chemical composition of surface layer differs. It is logical to assume that sorption ability of synthesized organosilicas depends on the structure of chemically grafted β -cyclodextrin molecules, which, obviously, are the main centers of Hg(II) and Cd(II) sorption.

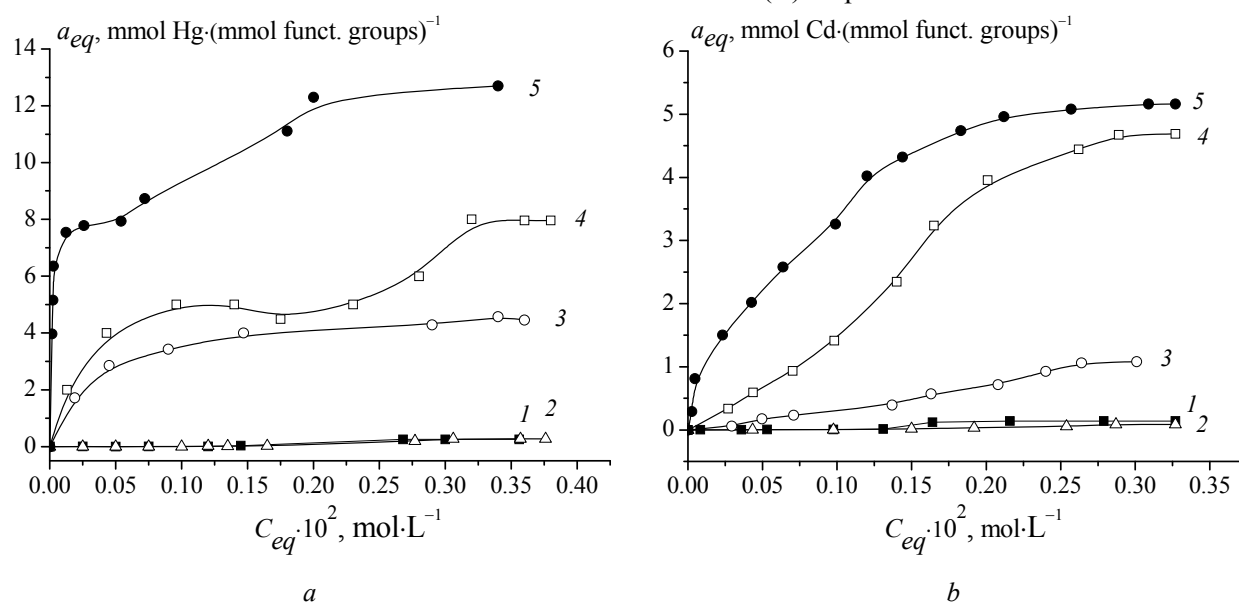


Fig. 3. Isotherms of mercury (II) (a) and cadmium (II) (b) sorption on silicas 1–5

Table 3. Characteristics of mercury (II) and cadmium (II) sorption from aqueous nitrate solutions

Silica	Specific cations sorption*, %		Distribution coefficient**, $\text{ml}\cdot\text{mg}^{-1}$		Molar ratio [cation]:[β -CD] on silica surface	
	Hg(II)	Cd(II)	Hg(II)	Cd(II)	Hg(II)	Cd(II)
1	25	14	4	7	0.25:1	0.14:1
2	27	9	4	5	0.28:1	0.09:1
3	460	110	315	125	5:1	1:1
4	800	470	153	200	8:1	4:1
5	1600	520	2941	340	14:1	5:1

* The concentration of silica functional groups was taken for 100 %

** The ratio of the quantity of adsorbed cations to its equilibrium concentration in a solution

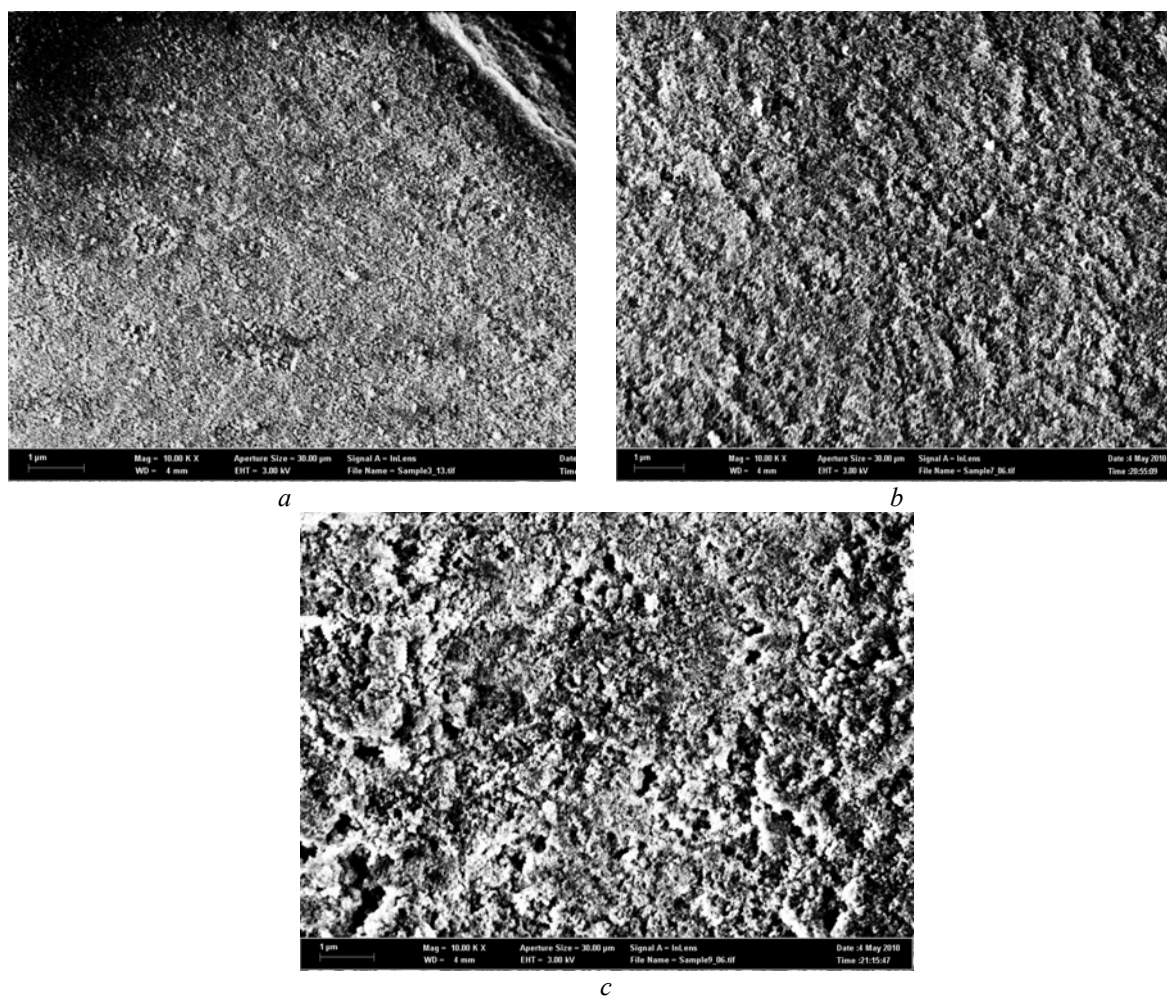


Fig. 4. SEM micrographs of silica 5 surface before (a) and after mercury (II) (b) and cadmium (II) (c) sorption

It should be also noted that according to the data of scanning electron microscopy (Fig. 4) the relief of surface of β -cyclodextrin-containing silicas has monotonous globular structure. After sorption of mercury (II) and cadmium (II) nitrates it becomes rougher; there is enlargement of the structural elements. This may be due to the formation of supramolecular structures (supermolecules) on the surface of β -cyclodextrin-containing silicas [30].

The sorption of Hg(II) from aqueous nitrate solutions at pH \sim 1 onto surface of silicas 1–5 occurs in the form of Hg^{2+} , and Cd(II) as Cd^{2+} and $\text{Cd}(\text{NO}_3)^+$ (Fig. 5). The participation of side functional groups of grafted β -cyclodextrins molecules in the sorption of Hg(II) and Cd(II) is confirmed by the IR spectroscopy results: the low-frequency shift (or disappearance) of characteristic absorption bands of the functional groups of the wide edge of β -CD and its

derivatives is observed after cations sorption (Table 4).

Earlier it was found [31] that upon contact of aqueous solutions of mercury nitrate (or cadmium) with β -cyclodextrin the formation of inclusion complexes of the “host–guest” type with 1:1 takes place by the entry of hydrated nitrate-ion into the inner cavity through the wide edge of the molecule of cyclic oligosaccharide. The high strength of the inclusion complex of “ β -CD– NO_3^- ” (stability constant $K_s = 1425 \pm 70 \text{ L}\cdot\text{mol}^{-1}$) may be a result of interaction between hydrated nitrate-ion and piranose oxygen of the β -CD molecule, and also geometric complementarity [12]: the volumes of upper part of inner cavity of β -CD ($V_{\text{cavity } \beta\text{-CD}} = 0.156 \text{ nm}^3$) and of hydrated nitrate-ion ($V_{\text{NO}_3^-} = 0.153 \text{ nm}^3$) are almost identical [32, 33]. It may be suggested that in the case of β -CD and its functional derivatives grafted onto silica surface aforementioned process will also occur, the more that a wide edge of grafted β -

cyclodextrin molecules remains accessible for the interaction with solution components (Scheme). Indeed, according to the data of chemical and elemental analysis, the decrease of quantity of NO_3^- in solutions of mercury (or cadmium) nitrates after contact with β -cyclodextrin-containing silicas is twice that quantity of adsorbed Hg (II) or Cd (II). This is proof of equivalent sorption of mercury (II) and cadmium (II) and nitrate-ions.

The silanol and aminopropyl groups of silicas under experimental conditions do not absorb mercury and cadmium cations, and after chemical grafting of β -cyclodextrins not their contribution to the electroconductivity of silica surface as well as the primary alcohol groups of narrow edge of β -cyclodextrins molecules [34, 35], whereby chemical attachment of β -CDs to the surface of silica carriers is being realized. Thus, only chemically attached β -cyclodextrins, namely their inner cavity and side functional groups of wide edge of the molecules, are involved in mercury and cadmium nitrates sorption.

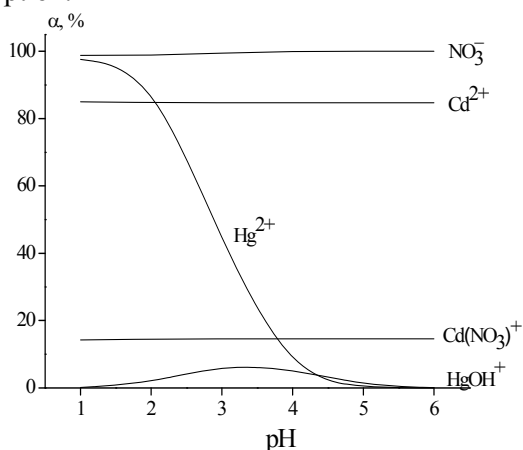


Fig. 5. Distribution curves of Hg(II) and Cd(II) forms in $0.1 \text{ mol}\cdot\text{L}^{-1}$ aqueous nitrate solutions as a function of pH

Sorption isotherms of mercury (II) on the synthesized β -cyclodextrin-containing silicas are well described by Langmuir equation (Fig. 6) for monolayer adsorption on localized sites of energetically uniform surface [24] throughout the studied concentration range. For cadmium (II) the experimental data are well approximated in the coordinates of Freundlich equation (Fig. 7) for sorption on heterogeneous surface [25]. The “surface heterogeneity” of the synthesized β -cyclodextrin-containing silicas for cadmium (II) sorption and its “homogeneity” for mercury (II) sorption are due to the fact that

mercury (II) is adsorbed as bivalent cations only, whereas cadmium (II) in form of Cd^{2+} and $\text{Cd}(\text{NO}_3)^+$ ions simultaneously.

The sequence of changing of the main parameters of mercury (II) and cadmium (II) sorption, which are given in Table 5, allows to place the studied β -cyclodextrin-containing silicas in a sequence: silica 3 < silica 4 < silica 5 according to its sorption affinity to mercury and cadmium cations.

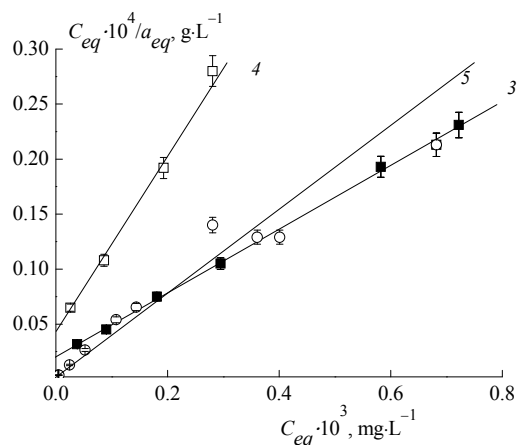


Fig. 6. Isotherms of mercury (II) sorption on silicas 3–5 (in coordinates of Langmuir equation)

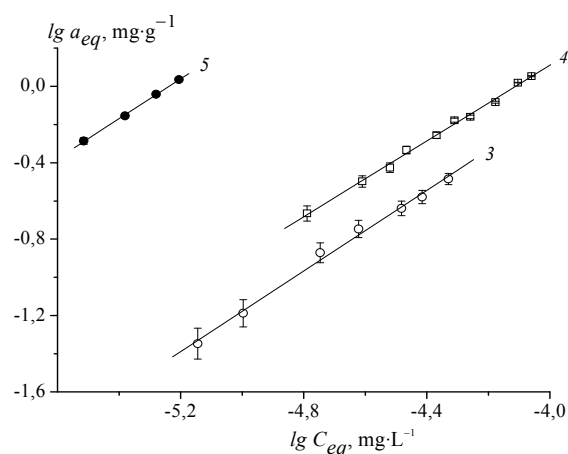


Fig. 7. Isotherms of cadmium (II) sorption on silicas 3–5 (in coordinates of Freundlich equation)

According to theory of hard and soft acids and bases [36, 37], the cations of mercury and cadmium are “soft” acids, and Hg^{2+} is “softer” acid than Cd^{2+} [38]. “Soft” acids form, as a rule, strong complexes with “soft” bases [36–38], whereas “hard” acids with “hard” bases. Earlier it was demonstrated that the main centers of mercury (II) and cadmium (II) sorption on surface of β -cyclodextrin-containing silicas are grafted

molecules of cyclic oligosaccharide which differ by chemical nature of side functional groups. The “softness” of side functional groups of the wide edge of β -cyclodextrins increases in order: secondary alcohol < bromoacetyl < thiosemicarbazido-acetyl groups [36–38]. Thus, it can be supposed that “soft” cations of mercury (II) and cadmium (II) will be forming preferably strong complexes with bromoacetyl and thiosemicarbazidoacetyl side groups (“soft” bases) of grafted oligosaccharide molecules. This is

indeed observed in the experiment. From theory of hard and soft acids and bases the contribution of inner cavity of β -CD molecules, occupied by “hard” nitrate-ion [36], to Hg(II) and Cd(II) sorption seems hardly probable. Most likely, the electroneutrality of inner cavity of β -CD, blocked by nitrate-ions, will be achieved by the interaction with “hard” acid, for example, nitric acid protons, those concentration in solutions with pH~1 is significantly higher than that of mercury and cadmium cations.

Table 4. The data of IR spectra of organosilicas before and after mercury (II) and cadmium (II) sorption

Silica	Characteristic absorption bands of IR spectra, cm^{-1}					
	before sorption		after Hg(II) sorption		after Cd(II) sorption	
1	3750	$\nu(\text{SiO-H})$ – silanol groups	3750	$\nu(\text{SiO-H})$ – silanol groups	3750	$\nu(\text{SiO-H})$ – silanol groups
2	3375 3310 1570 2955 2880 1415	$\nu_{\text{as}}(\text{N-H})$, $\nu_{\text{s}}(\text{N-H})$, $\delta(\text{N-H})$ – primary amino groups $\nu_{\text{as}}(\text{C-H})$, $\nu_{\text{s}}(\text{C-H})$, $\delta(\text{C-H})$ – methylene groups	3375 3310 1525 2955 1415	$\nu_{\text{as}}(\text{N-H})$, $\nu_{\text{s}}(\text{N-H})$, $\delta(\text{N-H})$ – primary amino groups $\nu_{\text{as}}(\text{C-H})$, $\delta(\text{C-H})$ – methylene groups	3315 3280 1520 2955 1415	$\nu_{\text{as}}(\text{N-H})$, $\nu_{\text{s}}(\text{N-H})$, $\delta(\text{N-H})$ – primary amino groups $\nu_{\text{as}}(\text{C-H})$, $\delta(\text{C-H})$ – methylene groups
3	3380 1590 1490 3290 2950 2880 1460	$\nu_{\text{as}}(\text{N-H})$, $\delta(\text{N-H})$ – primary amino groups $\delta(\text{N-H})$ – secondary amino groups $\nu_{\text{s}}(\text{O-H})$ – secondary alcohol groups of β -CD $\nu_{\text{as}}(\text{C-H})$, $\nu_{\text{s}}(\text{C-H})$, $\delta(\text{C-H})$ – methylene groups	3380 1525 3290 2950 1380	$\nu_{\text{as}}(\text{N-H})$, $\delta(\text{N-H})$ – primary amino groups $\nu_{\text{s}}(\text{O-H})$ – secondary alcohol groups of β -CD $\nu_{\text{as}}(\text{C-H})$, $\delta(\text{C-H})$ – methylene groups	3380 1525 3290 2950 1400	$\nu_{\text{as}}(\text{N-H})$, $\delta(\text{N-H})$ – primary amino groups $\nu_{\text{s}}(\text{O-H})$ – secondary alcohol groups of β -CD $\nu_{\text{as}}(\text{C-H})$, $\delta(\text{C-H})$ – methylene groups
4	3380 1540 1490 3290 2965 2880 1455 1755 680	$\nu_{\text{as}}(\text{N-H})$, $\delta(\text{N-H})$ – primary amino groups $\delta(\text{N-H})$ – secondary amino groups $\nu_{\text{s}}(\text{O-H})$ – secondary alcohol groups of β -CD $\nu_{\text{as}}(\text{C-H})$, $\nu_{\text{s}}(\text{C-H})$, $\delta(\text{C-H})$ – methylene groups $\nu(\text{C=O})$ – bromoacetyl groups $\nu(\text{C-Br})$ – bromoacetyl groups	3380 1530 1490 3290 2965 2880	$\nu_{\text{as}}(\text{N-H})$, $\delta(\text{N-H})$ – primary amino groups $\delta(\text{N-H})$ – secondary amino groups $\nu_{\text{as}}(\text{C-H})$, $\nu_{\text{s}}(\text{C-H})$ – methylene groups	3400 1530 1490 2965 2880	$\nu_{\text{as}}(\text{N-H})$, $\delta(\text{N-H})$ – primary amino groups $\delta(\text{N-H})$ – secondary amino groups $\nu_{\text{as}}(\text{C-H})$, $\nu_{\text{s}}(\text{C-H})$ – methylene groups
5	2970 2880 1455 1540 1470 1435	$\nu_{\text{as}}(\text{C-H})$, $\nu_{\text{s}}(\text{C-H})$, $\delta(\text{C-H})$ – methylene groups $\delta(\text{N-H})$ – primary amino groups $\nu(-\text{N-C-N-})$ – thiosemicarbazido-acetyl groups $\nu(\text{C=S})$ – thiosemicarbazidoacetyl groups	2970 2880 1520	$\nu_{\text{as}}(\text{C-H})$, $\nu_{\text{s}}(\text{C-H})$ – methylene groups $\delta(\text{N-H})$ – primary amino groups	2970 2880 1525	$\nu_{\text{as}}(\text{C-H})$, $\nu_{\text{s}}(\text{C-H})$ – methylene groups $\delta(\text{N-H})$ – primary amino groups

Table 5. Langmuir and Freundlich parameters for mercury (II) and cadmium (II) sorption on β -cyclodextrin-containing silicas

Silica	Langmuir coefficients				Freundlich coefficients		
	$K_L \times 10^{-4}$, $L \cdot mg^{-1}$	a_m , $mg \cdot g^{-1}$	R_L	R^2	$1/n$	K_F , $mg \cdot g^{-1}$	R^2
Hg(II)							
3	1.44±0.07	34±2.0	0.65±0.03	0.99	0.003	1.58±0.08	0.96
4	1.88±0.09	12.65±0.6	0.67±0.03	0.99	0.0023	1.29±0.06	0.97
5	33±1	21.74±1.0	0.47±0.2	0.99	5.88	2.03±0.10	0.89
Cd(II)							
3	0.37±0.02	1.77±0.1	0.97±0.06	0.67	0.80	3.90±0.23	0.99
4	0.10±0.06	14.57±0.8	0.99±0.06	0.26	1.00	4.30±0.26	0.99
5	2.61±0.15	4.99±0.3	0.92±0.05	0.95	1.25	5.50±0.33	0.99

As it is seen from Table 2, the kinetic processes of mercury (II) and cadmium (II) sorption depends on the chemical nature of cations being adsorbed and functional substituents in the molecules of grafted β -cyclodextrins. Thus, silica 3 has on the surface only one type of active sites – secondary alcohol groups of wide edge of β -CD molecules contributing to mercury (II) and cadmium (II) sorption. The pseudo-second order of reaction for cadmium (II) indicates that sorption of mono- and bivalent cadmium cations proceeds with distinguishable rates under experimental conditions.

The pseudo-second order of reaction for mercury (II) sorption onto silicas 4 and 5 is explained by the presence of two types of active sites, namely, “soft” bromoacetyl (or thiosemicarbazidoacetyl) groups, owing to which significant growth of mercury (II) sorption as

compared with silica 3 is observed, and residual secondary alcohol groups. β -Cyclodextrin has 14 side secondary alcohol groups, placed on wide edge of its toroidal molecule [11]. The ratio [Hg(II)]:[β -CD] (Table 3) reaching to 14 for silica 5 is proof that mercury cations sorption takes place not only on “soft” active centers, but also on residual secondary alcohol groups. Only “soft” centers of silicas 4 and 5 surface participate, apparently, in sorption of less “soft” cadmium (II), and therefore the reaction has pseudo-first order (Fig. 2). The molar ratio [Cd (II)]:[β -CD] equals 4 and 5, correspondingly.

The chemical composition of supramolecular structures (supermolecules), which are formed on the surface of β -cyclodextrin-containing silicas 3–5 as a result of mercury and cadmium sorption, is given in Table 6. Presented data are in good agreement with theory of hard and soft acids and bases.

Table 6. Chemical composition of surface supramolecular structures after sorption of mercury (II) and cadmium (II) nitrates on β -cyclodextrin-containing silicas from $10^{-3} \text{ mol} \cdot \text{L}^{-1}$ aqueous solution with pH~1

Silica	Chemical composition of supramolecular structures	
3	$C_{42}H_{70}O_{34} \cdot 5 Hg(NO_3)_2$	$C_{42}H_{70}O_{34} \cdot Cd(NO_3)_2$
4	$C_{98}H_{112}O_{53}S_6Br_9 \cdot 8 Hg(NO_3)_2$	$C_{98}H_{112}O_{53}S_6Br_9 \cdot 4 Cd(NO_3)_2$
5	$C_{107}H_{148}O_{53}S_{15}N_{27} \cdot 14 Hg(NO_3)_2$	$C_{107}H_{148}O_{53}S_{15}N_{27} \cdot 5 Cd(NO_3)_2$

CONCLUSIONS

Nanoporous β -cyclodextrin-containing silicas, which are various functional substituents of the wide edge of attached cyclic oligosaccharide molecules, have been synthesized.

Sorption of mercury (II) and cadmium (II) from aqueous solutions of corresponding nitrates

with pH~1 has been studied. It has been proved that simultaneously with sorption of mercury and cadmium cations onto surface of organosilicas the equimolar nitrate-ions uptake takes place.

Active surface centers of β -cyclodextrin-containing silicas, which are responsible for Hg^{2+} , Cd^{2+} , $Cd(NO_3)^+$ and NO_3^- sorption, have been ascertained. The formation of surface

supramolecular structures (supermolecules), which chemical composition depends on the nature of cations being adsorbed and functional substituents in the molecules of attached β -cyclodextrins, has been recognized.

Based on the data of scanning electron microscopy, spectral, chemical, elemental and thermogravimetric analysis of organosilicas before and after mercury (II) and cadmium (II) sorption, and the processing of the sorption results using Langmuir, Freundlich and Lagergren models the assignment of peculiarities of interaction of mercury and cadmium nitrates with functional nanoporous silicas has been given.

REFERENCES

1. *Government sanitary standard and rules "Sanitary orders for drinking water, intended for human use"* DSanPiN 2.2.4-171-10. – Kyiv: Ministry of public health protection of Ukraine order N 400, 12.05.2010 // Official Bulletin of Ukraine. – 2010. – N 51. – 99 p. (in Ukraine).
2. *Kutsenko S.A.* Basics of Toxicology. – Saint-Petersburg: Foliant, 2004. – 715 p. (in Russian).
3. *Scherbov D.P., Matveets M.A.* Analytical Chemistry of Cadmium. – Moscow: Nauka, 1973. – 255 p. (in Russian).
4. *Amphlett C.B.* Inorganic Ion Exchangers. – Amsterdam: Elsevier, 1964. – 141 p.
5. *Marhol M.* Ion Exchangers in Analytical Chemistry. Their Properties and Use in Inorganic Chemistry. – Prague: Academia, 1982. – 520 p.
6. *Ionites in Chemical Technology* / Eds. B.P. Nikol'skiy and P.G. Romankov. – Leningrad: Khimiya, 1982. – 416 p. (in Russian).
7. *Myasoedova G.V., Savvin S.B.* Chelating Sorbents. – Moscow: Nauka, 1984. – 172 p. (in Russian).
8. *Tertykh V.A., Belyakova L.A.* Chemical Reactions with Participation of Silica Surface. – Kiev: Naukova Dumka, 1991. – 261 p. (in Russian).
9. *Vansant E.F., Van Der Voort P., Vrancken K.C.* Characterization and Chemical Modification on the Silica Surface. – Amsterdam: Elsevier, 1995. – 556 p.
10. *Jal P.K., Patel S., Mishra B.K.* Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metal ions // *Talanta*. – 2004. – V. 62. – P. 1005–1028.
11. *Szejtli J.* Introduction and general overview of cyclodextrin chemistry // *Chem. Rev.* – 1998. – V. 98, N 5. – P. 1743–1752.
12. *Lehn J.M.* Supramolecular Chemistry. Concepts and Perspectives. – Weinheim-New York-Basel-Cambridge-Tokyo: VCH Verlagsgesellschaft, 1995. – 271 p.
13. *Steed J.W., Atwood J.L.* Supramolecular Chemistry. – Chichester-New York-Weinheim-Brisbane-Singapore-Toronto: John Wiley&Sons, 2000. – 990 p.
14. *Iler R.K.* The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemistry of Silica. – New York: Wiley-Interscience, 1979. – 866 p.
15. *Kiselev A.V.* Intermolecular Interactions in Adsorption and Chromatography. – Moscow: Vysshaya Shkola, 1986. – 360 p. (in Russian).
16. *Belyakova L.A., Kazdobin K.A., Belyakov V.N. et al.* Synthesis and properties of supramolecular systems based on silica // *J. Colloid Interface Sci.* – 2005. – V. 283. – P. 488–494.
17. *Belyakova L.A., Lyashenko D.Yu., Varvarin A.M. et al.* Features of the interaction of silica with tosyl- β -cyclodextrin // *Ukr. Chem. Journal*. – 2005. – V. 71, N 8. – P. 86–92 (in Russian).
18. *Belyakova L.A., Varvarin A.M., Lyashenko D.Yu., Khora O.V.* Designing adsorption centres for biological active molecules on a silica surface // *Ads. Sci. Technol.* – 2005. – V. 23, N 9. – P. 703–719.
19. *Experimental Methods in Adsorption and Molecular Chromatography* / Eds. A.V. Kiselev and V.P. Dreving. – Moscow: MGU Publisher, 1973. – 448 p. (in Russian).
20. *Belyakova L.A., Besarab L.N., Roik N.V. et al.* Designing of the centers for adsorption of bile acids on a silica surface // *J. Colloid Interface Sci.* – 2006. – V. 294. – P. 11–20.
21. *Goldstein J. I., Yakowitz H.* Practical Scanning Electron Microscopy. Electron and Ion Microprobe Analysis. – New York: Plenum, 1975. – 582 p.
22. *Schwarzenbach G., Flashka H.* Die Komplexometrische Titration. – Stuttgart: Ferdinand Enke, Verlag, 1965. – 360 p.
23. *Bagdasarov K.N., Kovalenko P.N., Shemyakina M.A.* A study of indium, cadmium and bismuth complexes with xylenol orange and their use for the photometric determination of these elements // *J. Analyt. Chem.* – 1968. – V. 23, N 4. – P. 515–520 (in Russian).
24. *Langmuir I.* The adsorption of gases on plane surfaces of glass, mica and platinum // *J. Am. Chem. Soc.* – 1918. – V. 40, N 9. – P. 1361–1403.
25. *Freundlich H., Heller W.J.* The adsorption of *cis*- and *trans*-azobenzene // *J. Am. Chem. Soc.* – 1939. – V. 61, N 8. – P. 2228–2230.
26. *Gupta S.S., Bhattacharyya K.G.* Adsorption of Ni(II) on clays // *J. Colloid Interface Sci.* – 2006. – V. 295, N 1. – P. 21–32.
27. *Belyakova L.A., Lyashenko D.Yu., Shvets O.M.* Influence of the surface structure of β -cyclodextrin-containing silica on the adsorption of mercury nitrate from dilute solutions // *Russ. J. Phys. Chem. A.* – 2010. – V. 84, N 4. – P. 656–660.
28. *Belyakova L.A., Shvets O.M.* Adsorption and complexing properties of silica modified with β -

- cyclodextrin // Chemistry, Physics and Technology of Surface. – 2010. – V. 1, N 3. – P. 274–280.
29. Schindler P., Kamber G.R. Die Acidität von Silanolgruppen. Vorläufige Mitteilung // Helv. Chim. Acta. – 1968. – V. 51, N 7. – S. 1781–1786.
 30. Fenelonov V.B. Introduction into Physical Chemistry of Formation of Supramolecular Structure of Adsorbents and Catalysts. – Novosibirsk: SB RAS, 2004. – 442 p. (in Russian).
 31. Belyakova L.A., Lyashenko D.Yu., Shvets O.M. Interaction of β -cyclodextrins with nitrates of cadmium (II) and mercury (II) // Coll. Chemistry, Physics and Technology of Surface. – 2009. – Iss. 15. – P. 80–86 (in Russian).
 32. Belyakova L.A., Lyashenko D.Yu. Complex formation between benzene carboxylic acids and β -cyclodextrin // J. Appl. Spectrosc. – 2008. – V. 75, N 3. – P. 314–318.
 33. Belyakova L.A., Lyashenko D.Yu., Shvets O.M. Designing of the nanosized centers for adsorption of mercury (II) on a silica surface // Nanomaterials and Supramolecular Structures. Physics, Chemistry, and Applications / Eds: A.P. Shpak and P.P. Gorbyk. – Springer, 2009. – P. 247–258.
 34. Dzyazko Yu.S., Belyakova L.A. The influence of the functional groups on the electrical conductivity of silica // Ukr. Chim. Zhurnal. – 2009. – V. 75, N 10. – P. 77–83 (in Russian).
 35. Dzyazko Yu.S., Belyakova L.A., Lyashenko D.Yu. Diagnostics of functional organosilicas surface by impedance spectroscopy // Chemistry, Physics and Technology of Surface. – 2011. – V. 2, N 3. – P. 242–248 (in Russian).
 36. Pearson R.G. Hard and soft acids and bases. Part I. Fundamental principles // J. Chem. Educ. – 1968. – V. 45. – P. 581–587.
 37. Pearson R.G. Hard and soft acids and bases. Part II. Underlying theories // J. Chem. Educ. – 1968. – V. 45, N 10. – P. 643–648.
 38. Marcus Y., Kamlet M. J., Taft R. W. Linear solvation energy relationships. Standard molar Gibbs free energies and enthalpies of transfer of ions from water into nonaqueous solvents // J. Phys. Chem. – 1988. – V. 92. – P. 3613–3622.

Received 05.10.2012, accepted 15.10.2012

Нові нанопористі β -циклодекстринвмісні органокремнеземи для сорбції нітратів важких металів

Л.О. Бєлякова, О.М. Швець, Д.Ю. Ляшенко

Інститут хімії поверхні ім. О.О. Чуйка Національної академії наук України
вул. Генерала Наумова, 17, Київ, 03164, Україна, mila.belyakova@gmail.com

Синтезовані нанопористі β -циклодекстринвмісні кремнеземи, які відрізняються функціональними замісниками широкого краю прищеплених молекул циклічного олігосахариду. Доведено утворення на поверхні органокремнеземів супрамолекулярних структур (супермолекул), хімічний склад яких залежить від природи катіонів, що вилучаються, і функціональних замісників у молекулах прищеплених β -циклодекстринів. Надано тлумачення особливостей взаємодії нітратів ртуті та кадмію з синтезованими β -циклодекстринвмісними кремнеземами з позицій теорії жорстких і м'яких кислот та основ.

Новые нанопористые β -циклодекстринсодержащие органокремнеземи для сорбции нитратов тяжелых металлов

Л.А. Белякова, А.Н. Швец, Д.Ю. Ляшенко

Институт химии поверхности им. А.А. Чуйко Национальной академии наук Украины
ул. Генерала Наумова, 17, Киев, 03164, Украина, mila.belyakova@gmail.com

Синтезированы нанопористые β -циклодекстринсодержащие кремнеземи, отличающиеся функциональными заместителями широкого края привитых молекул циклического олигосахаридов. Доказано образование на поверхности органокремнеземов супрамолекулярных структур (супермолекул), химический состав которых зависит от природы сорбируемых катионов и функциональных заместителей в молекулах привитых β -циклодекстринов. Дана интерпретация особенностей взаимодействия нитратов ртути и кадмия с синтезированными β -циклодекстринсодержащими кремнеземами с позиций теории жестких и мягких кислот и оснований.