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FUNCTIONAL b-CYCLODEXTRINS AS THE ACTIVE CENTRES ON THE SILICA SURFACE FOR TOXIC IONS SORPTION

Nanoporous β-cyclodextrin-bonded silica, which differ by functional substituents of the wide edge of attached cyclic oligosaccharide molecules, were synthesized. The structure and chemical composition of the surface of nanoporous organosilicas were found. Sorption of mercury (II), cadmium (II), and zinc (II) from dilute acidic nitrate solutions by nanoporous organosilicas was studied. Sorption results were analyzed using Lagergren's kinetic model and Langmuir and Freundlich models for equilibrium adsorption. The interpretation of interaction features of mercury, cadmium and zinc nitrates with β-cyclodextrin-bonded silica was done according to the theory of hard and soft acids and bases.

INTRODUCTION. Heavy metals and their compounds as technological products of human activity are the main pollutants of the environment [1–3]. They are non-biodegradable toxic substances [3], so the problem of its sorption extraction is still relevant. Another important task is to develop methods of express-analysis of heavy metal impurities in drinking and waste waters, soils, biological fluids, as well as in food products of animal and vegetable origins, medicines, cosmetics and personal hygiene items.

The problem of extraction of heavy metals from water and aqueous solutions with organic and inorganic ion exchange materials is only partially solved, because the efficiency of ion exchangers is significantly reduced with the decrease of toxic impurities amounts [4–6].

Adsorbents, whose action is based on the complexation process [7, 8] and molecular recognition [9–12], can be promising for the extraction and chemical analysis of toxic metal impurities. These adsorbents, in addition to high sorption specificity, must have the uniform chemical composition of functional groups, the high kinetic parameters of sorption, and, therefore, an extensive network of transport pores, and also the texture, which does not swell in water and organic solvents. High demands are made on the hydrolytic, thermal, bacterial and radiation stability of sorption materials.

Disperse amorphous silica meet the above requirements. In addition, they have a high reactivity of the surface sites. Therefore, silica is widely used as initial matrices in the synthesis of complex formation adsorbents [13–15]. This offers great opportunities for directional design of various functional groups and supramolecular structures with high specificity and selectivity on the silica surface. For these purposes, the chemical immobilization of functional macro cyclic compounds, such as crown ethers, calixarenes, cyclodextrins are increasingly used [16–25].

This paper presents the results of Hg(II), Cd(II), and Zn(II) sorption on disperse silica chemically modified with β-cyclodextrins, which differ in chemical nature of side functional groups of the wide edge of cyclic oligosaccharide molecules.

EXPERIMENTAL PART. Nanoporous highly disperse silica — silochrome C-120 (Russia) with specific surface area of 133 m^2/g, and particle size of 0.3–0.5 mm was used as starting material.

β-Cyclodextrin (β-CD, from Fluka, purity 99 %), (3-aminopropyl)-triethoxysilane, dimethylchlorosilane, 4-toluenesulfonyl chloride and thiosemicarbazide (from Merck, purity 99 %), were used without additional purification. Toluene, pyridine and acetone (all from Reakhim, pure analytical) were distilled and dried for 72 h by use of activated 4 A molecular sieves.

Chemical composition of the silica surface was determined by elemental analysis (Elemental Analyzer EA 1110), potentiometric titration (Ionometer I-120.1), and also on chemisorption of dimethylchlorosilane [14].

Parameters of the porous structure of starting and modified silicas were calculated from low-temperature nitrogen ad-desorption isotherms measured by Sorptometer Kelvin 1042.

Infrared transmission spectra of organosilicas were registered in the frequency range 4000–500 cm^{-1} using a Thermo Nicolet Nexus FT-IR spectro-

photometer. The plates of ~ 30 mg each were compacted under a pressure of 10^8 Pa for the recording IR spectra.

UV absorption spectra of mercury, cadmium, and zinc nitrate solutions, and nitric acid were recorded by use a spectrophotometer Specord M-40 in the wavelength range 220—350 nm.

Sorption of mercury (II), cadmium (II) and zinc (II) cations onto organosilicas 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 aqueous solutions of corresponding nitrates 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 [26]. The amounts of Cd(II) and Zn(II) were determined using xylenol orange as a reagent by the intensity of absorption band at $\lambda_{\max}$ 576 and 570 nm on a Perkin–Elmer Lambda 35 spectrophotometer and Specord M-40, respectively [27].

The relative content of various forms of mercury (II), cadmium (II) and zinc (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).

Lagergren's kinetic models for the processes of pseudo-first and pseudo-second orders were used for analysis of the kinetic curves of Hg(II), Cd(II) and Zn(II) sorption [28]. Integral form of Lagergren's kinetic model for pseudo-first order processes is expressed by the equation:

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

where a_t and a_{eq} are the adsorption at time t and at the equilibrium state, mg/g; k_1 is the rate constant of adsorption, 1/min.

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

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

where k_2 is the rate constant of adsorption, g/mg·min.

The results of equilibrium sorption of Hg(II), Cd(II) and Zn(II) have been analyzed by use of equations of Langmuir isotherm [29]:

$$\frac{C_{eq}}{a_{eq}} = \frac{1}{K_L} \cdot a_m + \frac{1}{a_m} \cdot C_{eq} ,$$

where C_{eq} is the equilibrium concentration of adsorptive, mg/L; a_{eq} is the equilibrium adsorption, mg/g; K_L is Langmuir constant characterizing adsorption energy, L/mg; a_m is the adsorption capacity of monolayer, mg/g;

and Freundlich isotherm [30]:

$$\lg a_{eq} = \lg K_F + \frac{1}{n} \cdot C_{eq} ,$$

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

The separation factor R_L [28] was calculated by the formula:

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

where C_0 is the initial concentration of the adsorptive, mg/L; K_L is Langmuir constant, L/mg.

RESULTS AND DISCUSSION. Starting silica material (silochrome) before chemical modification was heated in air at 400 °C for 2 h to remove impurities of organic compounds and adsorbed water. Concentration of free silanol groups on the surface of preheated silica was 0.4 mmol/g.

Aminopropylsilica was prepared by reaction of electrophilic substitution between silanol groups of silica surface and ethoxy groups of (3-aminopropyl)-triethoxysilane. Silica was placed into a three-necked reactor supplied with a stirrer and a reflux condenser, was suspended in a small amount of toluene at room temperature for 40 min, then (3-aminopropyl)-triethoxysilane was added. The reaction mixture was stirred at 110 °C for 6 h. Then the solid phase was washed on a porous glass filter with toluene until the absence of silane (absence of a violet color on addition of ninhydrin), then with acetone, distilled water (for hydrolysis of the ether groups), and again with acetone. Obtained aminopropylsilica was dried in the air at 150 °C during 6 h. The concentration of aminopropyl groups equals 0.4 mmol/g. The resulting organosilica was used for chemical grafting of β-cyclodextrin and its functional derivatives.

Mono-toluenesulfonyl-β-cyclodextrin was synthesized as described in [31]. Chemical immobilization of mono-toluenesulfonyl-β-cyclodextrin was realized by the reaction of electrophilic substitution between amino groups of aminopropylsilica and toluenesulfonyl groups of functional β-cyclodextrin.
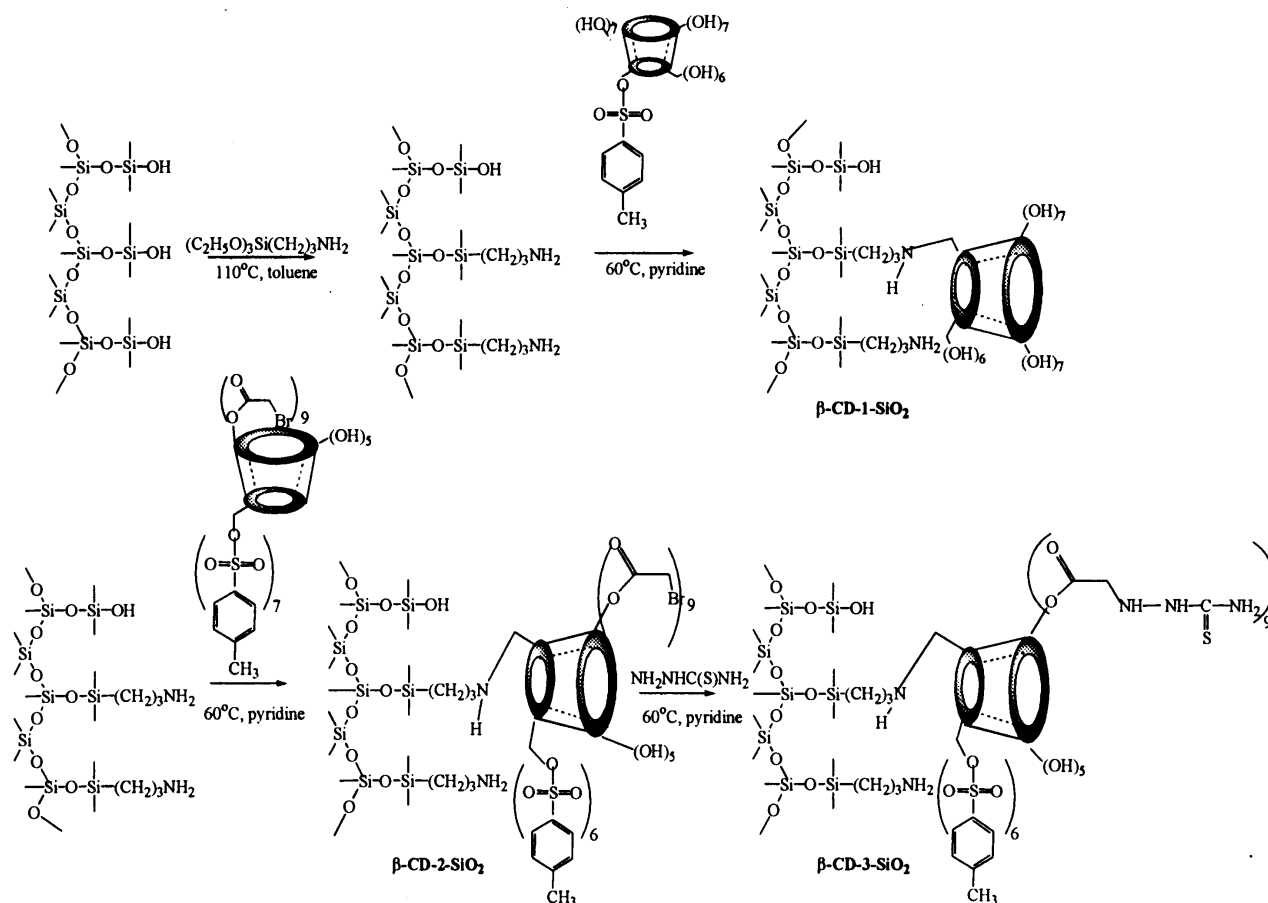
Fig. 1. Synthesis of β-CG-containing organosilicas.

Three-time excess of mono-tosyl-β-cyclodextrin was added to the suspension of aminopropylsilica in dried pyridine and kept at 60 °C for 96 h in the presence of triethylamine as a catalyst. Then modified silica was washed with pyridine and acetone. The concentration of grafted β-CD groups onto silica surface is 0.02 mmol/g (β-CD-1-SiO$_2$).

In a similar way organosilica chemically modified with bromoacetyl-β-cyclodextrin was prepared. The concentration of grafted β-CD groups onto silica surface is 0.01 mmol/g (β-CD-2-SiO$_2$).

The replacement of bromoacetyl groups of chemically attached β-CD for thiosemicarbazido-acetyl groups was realized under conditions of optimal running of surface reaction of nucleophilic substitution. The chemical reaction takes place at 110 °C; a solvent is dried toluene; reaction time is 6 h. The conversion degree of bromoacetyl groups to thiosemicarbazidoacetyl groups (β-CD-3-SiO$_2$) is 100 % (fig. 1).

The course of chemical reactions on the silica surface was proved by chemical analysis of the reaction products. The elemental and chemical analysis, potentiometric titration, data of IR spectroscopy, thermogravimetry, and the low-temperature nitrogen ad-desorption were used to determine the chemical composition and structure of the surface layer of β-CD-bonded silicas and their structural and sorption parameters (table 1).

Chemical modification of surface of the starting silica 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-bonded silicas remain highly disperse materials with nanosized pores (table 1). Therefore, it can be supposed that the sorption of mercury (II), cadmium (II), and zinc (II) onto β-CD-bonded silicas will not be complicated by inner diffusion.

In the acidic range in nitrate solutions Hg(II)

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Chemical composition of surface layer and structural characteristics of synthesized organosilicas

Organosilica	Elemental composition of organosilica surface layer, %					C^*, mmol/g	S, m^2/g	V, cm^3/g	d, nm
	H	C	N	Br	S				
Initial SiO$_2$						0.40	133	0.80	46
β-CD-1-SiO$_2$	0.40	1.60	0.40	—	—	0.02	98	0.58	29
β-CD-2-SiO$_2$	0.60	2.20	0.40	0.70	0.20	0.01	95	0.50	24
β-CD-3-SiO$_2$	0.65	2.20	0.80	—	0.50	0.01	90	0.42	17

* C – concentration of functional groups; S – specific surface; V – summary volume of pores; d – average diameter of pores.
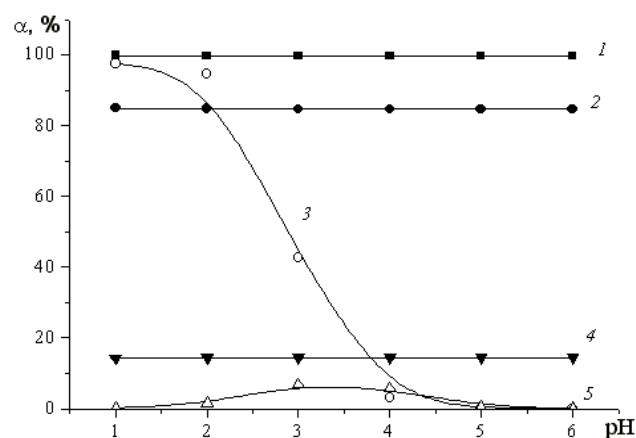

Fig. 2. Distribution curves of Zn^{2+}, Cd^{2+}, Hg^{2+}, Cd(NO$_3$)$^+$ and Hg(OH)$^+$ forms in 0.1 mol/L aqueous nitrate solutions as a function of pH (curves *1–5*, respectively).

exists mostly in the form of Hg^{2+}, Cd(II) — as Cd^{2+} and Cd(NO$_3$)$^+$, and Zn(II) — as Zn^{2+} (fig. 2).

Sorption equilibrium on the β-CD-silicas is reached already for 1–2 h of the contact with solutions of mercury, cadmium or zinc nitrates (fig. 3). The molar ratio of [metal] : [β-CD] is varied for mercury from 5 to 14, for cadmium from 1 to 5 and for zinc from 7 to 14. Sorption potential centres are functional groups of grafted β-CD molecules (fig. 1, table 2), the inner cavity of the cyclic oligosaccharide and residual aminopropyl groups of silica surface. However, aminopropyl groups of silica do not absorb mercury, cadmium or zinc cations under experimental conditions, and after the chemical immobilization of β-CDs they make no contribution to the electrical conductivity of the surface of organosilicas as well as the primary alcohol groups of the narrow edge of the grafted molecules of oligosaccharides. Thus, the real centres of heavy metals sorption
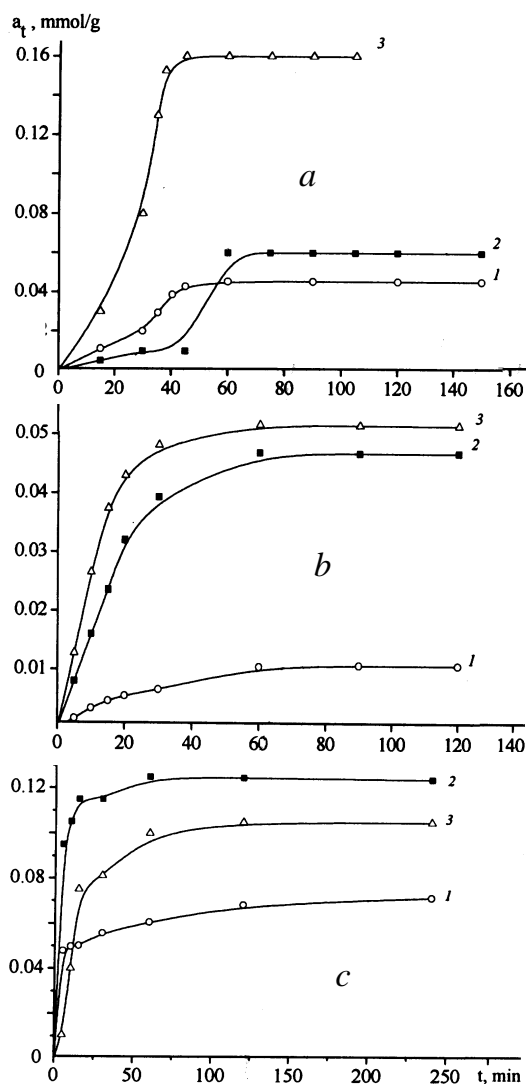

Fig. 3. Kinetic curves of mercury (II) (*a*), cadmium (II) (*b*), and zinc (II) (*c*) sorption on organosilicas β-CD-1-SiO$_2$—β-CD-3-SiO$_2$ (curves *1–3*, respectively).

T a b l e 2

Surface structure of functional b-cyclodextrin-containing silicas

Organosilica	Functional groups of wide edge of grafted β-CD molecules	
	Type	Number
β-CD-1-SiO$_2$	Secondary alcohol groups	14
β-CD-2-SiO$_2$	Secondary alcohol	5
	Bromoacetyl groups	9
β-CD-3-SiO$_2$	Secondary alcohol	5
	Thiosemicarbazidoacetyl groups	9

can be only the internal cavity of grafted β-CDs and side functional groups of wide edge of their torus-shaped molecules.

Symmetric absorption band with $\lambda_{max}= 302$ nm and $\varepsilon =294$ L/mol·cm, which belongs to the $n \rightarrow \pi^*$ chromophore transition for N=O [32] in the nitrate-anion, is present in the electronic spectra of aqueous solutions of mercury, cadmium, and zinc nitrates, and nitric acid also (fig. 4). The absorption band with $\lambda_{max}=302$ nm becomes asymmetric and its intensity increases dramatically ($\varepsilon =3100$ L/mol·cm) after adding β-CD, which has no characteristic absorption bands in the UV region. The content of nitrate-anions in equilibrium solutions decreases. This fact together with spectral changes of the chromophore N=O
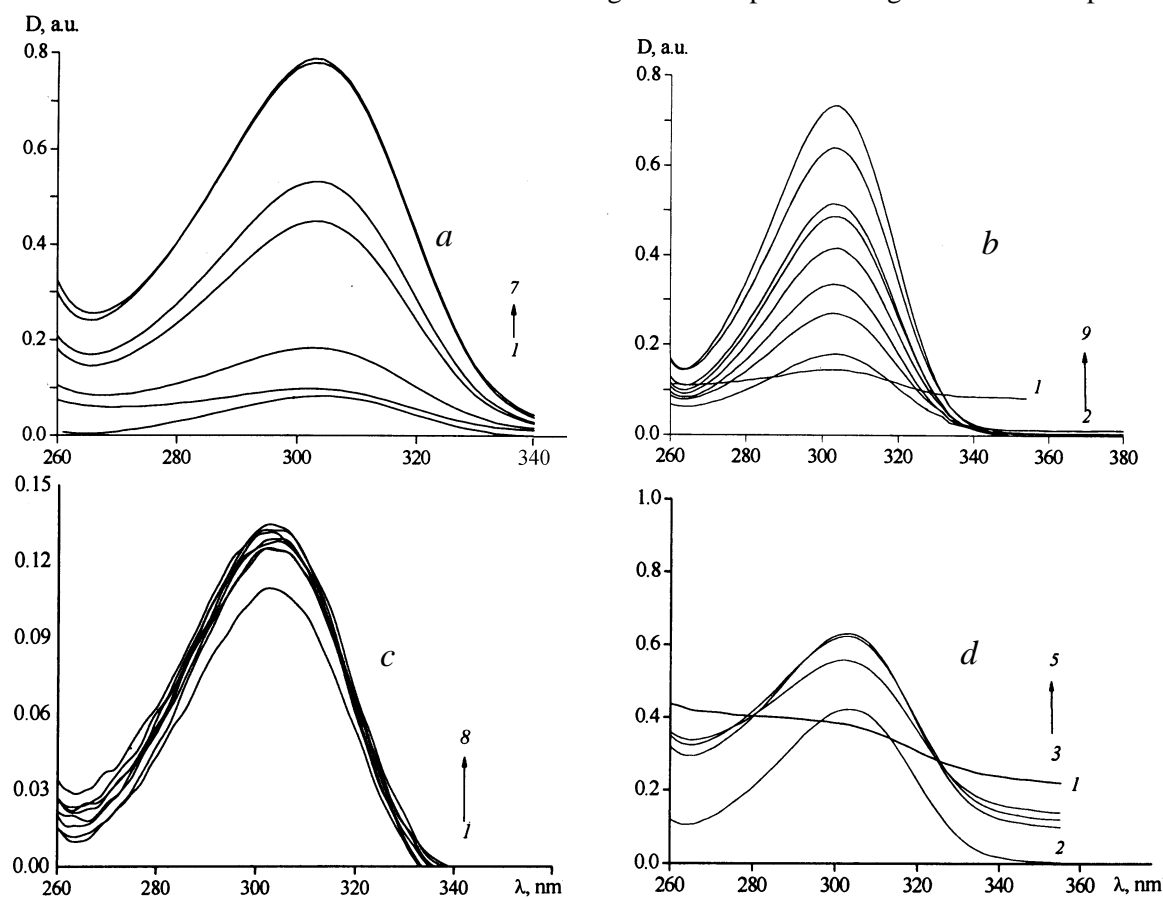

Fig. 4. UV absorption spectra of aqueous solutions of mercury (*a*), cadmium (*b*), zinc (*c*) nitrates and nitric acid (*d*), and also their binary solutions with β-cyclodextrin. *a* — 0.2·10^{-4} M Hg(NO$_3$)$_2$ solution (*1*), and binary solutions with molar ratio [β-CD]:[NO$_3^-$]=9:1 (*2*), 8:2 (*3*), 1:1 (*4*), 4:6 (*5*), 1:9 (*6*), 0.5:9.5 (*7*); *b* — 1.0·10^{-3} M Cd(NO$_3$)$_2$ solution (*1*), and binary solutions with molar ratio [β-CD]:[NO$_3^-$]=20:1 (*2*), 12:1 (*3*), 7.5:1 (*4*), 5:1 (*5*), 1:0.3 (*6*), 1:0.5 (*7*), 1:0.8 (*8*), 1.8:1 (*9*); *c* — 1.0·10^{-3} M Zn(NO$_3$)$_2$ solution (*1*), and binary solutions with molar ratio [β-CD]:[NO$_3^-$]=1:1 (*2*), 1:2 (*3*), 1:6 (*4*), 2:3 (*5*), 1:5 (*6*), 1:8 (*7*), 1:9 (*8*); *d* — 12.5·10^{-3} M β-CD solution (*1*), 1·10^{-3} M HNO$_3$ solution (*2*), and binary solutions with molar ratio [β-CD]:[NO$_3^-$]=1:6 (*3*), 2:1 (*4*), 1:1 (*5*).
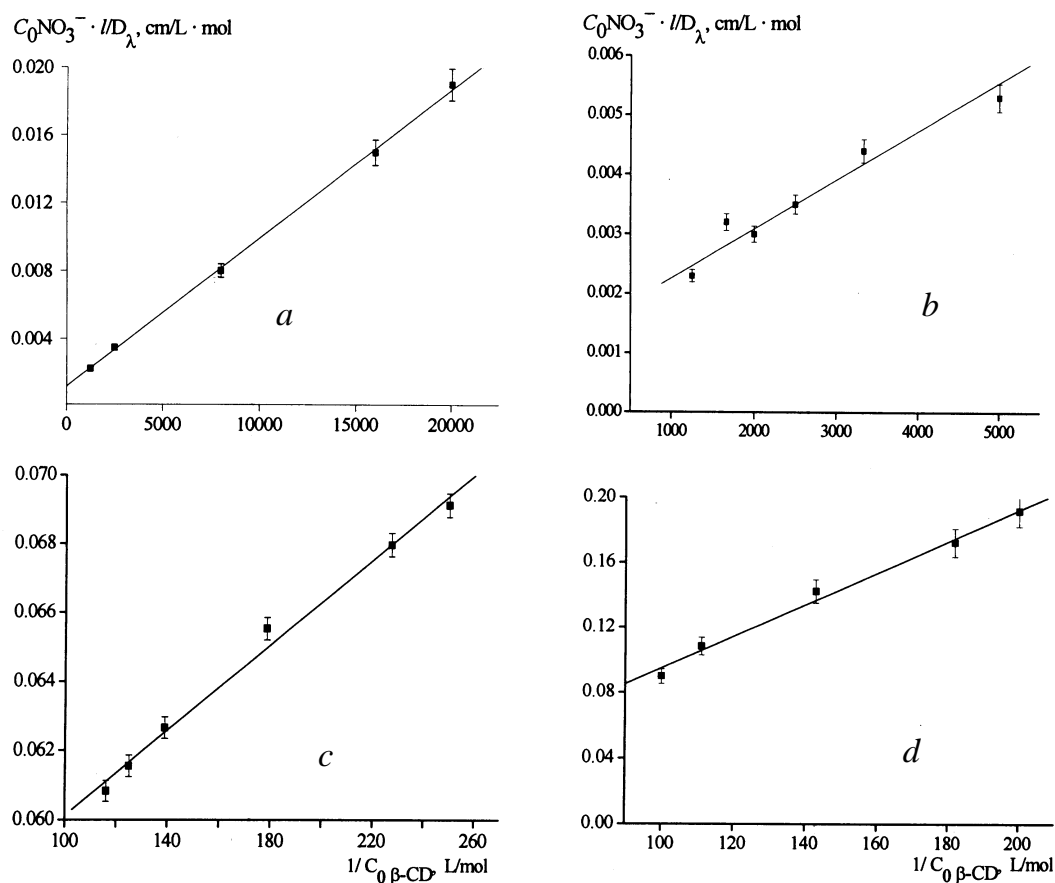
Fig. 5. Dependence of spectral characteristics of nitrate-anion on amount of β-cyclodextrin in aqueous solutions of mercury (*a*), cadmium (*b*), zinc (*c*) nitrates and nitric acid (*d*) in the coordinates of Beneshi–Hildebrand equation for inclusion complex of 1:1.

absorption band indicates interaction of NO_3^- with β-CD, namely the formation of the "host–guest" complexes in binary solutions containing β-cyclodextrin and nitrates (or nitric acid). The composition of formed inclusion complexes was determined by isomolar series method.

The experimental points in all cases lie on a straight line in the coordinates of Beneshi–Hildebrand equation [33] for "β-cyclodextrin—nitrate-anion" complex of 1:1 (fig. 5), and stability constants have similar values ($K_s = 1000$—1425 L/mol).

The formation of inclusion complexes, apparently, will also occur, for β-CD and its functional derivatives grafted onto silica surface, since the wide edge of grafted β-CD molecules remains accessible for solution components (fig. 1). It was found that surface inclusion complexes of the "host–guest" type with 1:1 are formed by the entry of hydrated nitra-

te-anion into the inner cavity through the wide edge of the molecule of cyclic oligosaccharide and interaction between hydrated nitrate-anion and piranose oxygen of the β-CD molecule, and also geometric complementarity: the volumes of upper part of inner cavity of β-CD ($V_{\beta\text{-CD cavity}} = 0.156$ nm^3) and of hydrated nitrate-anion ($V_{NO_3^-} = 0.153$ nm^3) are almost identical (fig. 6). This greatly complicates the sorption of heavy metals cations in the cavity of grafted β-CD molecules.

In addition, according to the data of chemical and elemental analysis, the decrease of NO_3^- quantity in solutions of mercury (or cadmium, or zinc) nitrates after contact with β-CD-bonded silicas is twice that amount of adsorbed cations. This is proof of equivalent sorption of mercury (II), cadmium (II), zinc (II) and nitrate-anions. Thus, the internal cavity of grafted molecules of cyclic oligosaccharides is not
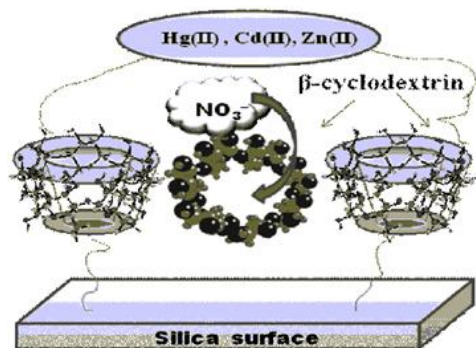
Fig. 6. Inclusion complexes of the "host–guest" type with 1:1.

involved in adsorption of mercury (or cadmium, or zinc) cations for steric reasons, and the only centres of their sorption are the side functional groups of wide edge of β-CD molecules.

In the analysis of the kinetic curves of mercury (II), cadmium (II), and zinc (II) sorption was used Lagergren's model for processes of pseudo-first and pseudo-second orders [28]. Lagergren's model for reactions of pseudo-first order describes well the sorption processes in which the adsorbate interacts with the surface active sites having the same chemical composition and structure. The model of 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 β-CD-1-SiO$_2$ is well fitted to linear form of Lagergren equation for pseudo-first order processes, but for cadmium (II) it corresponds to reaction of pseudo-second order. The sorption of Hg(II) onto silicas β-CD-2-SiO$_2$ and β-CD-3-SiO$_2$ fits to pseudo-second order processes model, whereas for Cd(II) it obeys Lagergren equation for pseudo-first order reactions (table 3, fig. 7). Kinetic curves of Zn(II) sorption for the β-CD-1-SiO$_2$ and β-CD-3-SiO$_2$ have pseudo-first order and pseudo-second order for β-CD-2-SiO$_2$. The rate constants of sorption of Hg (II), Cd(II) and Zn(II) have been calculated (table 3). Thus, the pseudo-first order of kinetic curves indicates that the sorption of one type of cations takes place on single type of surface active sites of β-CD-bonded silicas or on different nature centres, but with invisible rates of processes. Pseudo-second order of kinetic sorption curves corresponds to absorption of various cations (as for

cadmium) on single type of sorption centres, or sorption of a variety of cations on different centres of organosilica surface with significantly various rates. As it is seen from table 3, the kinetic processes of mercury (II), cadmium (II), and zinc (II) sorption depends on the chemical nature of cations being adsorbed and functional substituents in the molecules of grafted β-cyclodextrins. Thus, β-CD-1-SiO$_2$ has on the surface the only type of active sites — the secondary alcohol groups of wide edge of β-CD molecules contributing to mercury (II), cadmium (II) and zinc (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 β-CD-2-SiO$_2$ and β-CD-3-SiO$_2$ is explained by the presence of two types of active sites, namely, bromoacetyl (or thiosemicarbazidoacetyl) groups and residual secondary alcohol groups (fig. 1). As kinetic curves of Zn(II) sorption for the β-CD-1-SiO$_2$ and β-CD-3-SiO$_2$ have pseudo-first order, the secondary alcohols are the sorption centres of zinc (II) for β-CD-1-SiO$_2$, and the secondary alcohol and thiosemicarbazidoacetyl groups —for β-CD-3-SiO$_2$, as sorption on these centres have similar kinetic parameters. Kinetic curve of Zn (II) sorption in the case of β-CD-2-SiO$_2$ has pseu-

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Rate constants of mercury (II), cadmium (II) and zinc (II) sorption for processes of pseudo-first (k_1) and pseudo-second (k_2) orders

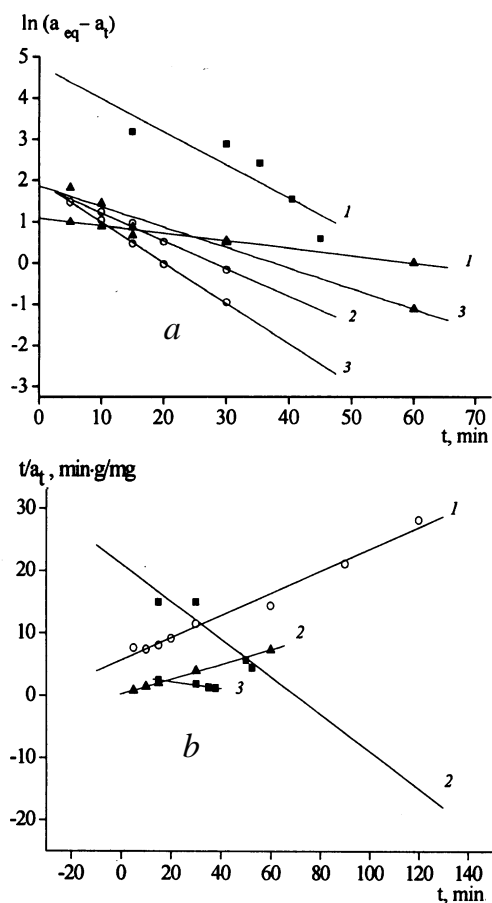| Organosilica	k_1, 1/min	R_1^2	k_2, g/mg·min	R_2^2
	Hg(II)			
β-CD-1-SiO$_2$	5.9 ± 0.3	0.92		
β-CD-2-SiO$_2$			0.020 ± 0.001	0.79
β-CD-3-SiO$_2$			0.016 ± 0.001	0.98
	Cd(II)			
β-CD-1-SiO$_2$			0.31 ± 0.02	0.99
β-CD-2-SiO$_2$	1.9 ± 0.1	0.99		
β-CD-3-SiO$_2$	2.0 ± 0.1	0.99		
	Zn(II)			
β-CD-1-SiO$_2$	0.018 ± 0.001	0.99		
β-CD-2-SiO$_2$			0.055 ± 0.003	0.99
β-CD-3-SiO$_2$	0.049 ± 0.003	0.98		

Fig. 7. Kinetic curves of mercury (■), cadmium (o), and zinc (Δ) sorption on silicas β-CD-1-SiO$_2$—β-CD-3-SiO$_2$ (lines *1–3*, respectively) in coordinates of Lagergren equations for processes of pseudo-first (*a*) and pseudo-second (*b*) orders.

do-second order and sorption of zinc (II) takes place with participation of the secondary alcohol and thiosemicarbazidoacetyl groups.

The results of equilibrium sorption study are presented in fig. 8. The silicas modified with β-CD and its functional derivatives adsorb mercury (II), cadmium (II) and zinc (II) already at low concentrations in a solution. Moreover, the sorption capacity of β-CD-bonded silicas exceeds the amount of chemically attached β-CD molecules in several times (table 1). It is logical to assume that sorption ability of synthesized organosilicas depends on the structure of chemically grafted β-CD molecules, which are the centres for Hg(II), Cd(II), and Zn(II) sorption.

The participation of side functional groups of grafted β-CDs molecules in sorption of Hg(II), Cd

(II) and Zn(II) is confirmed by the IR spectroscopy results: the low-frequency shift (or disappearance) of characteristic absorption bands of functional groups of the wide edge of β-CD and its derivatives is observed after cations sorption (table 4).
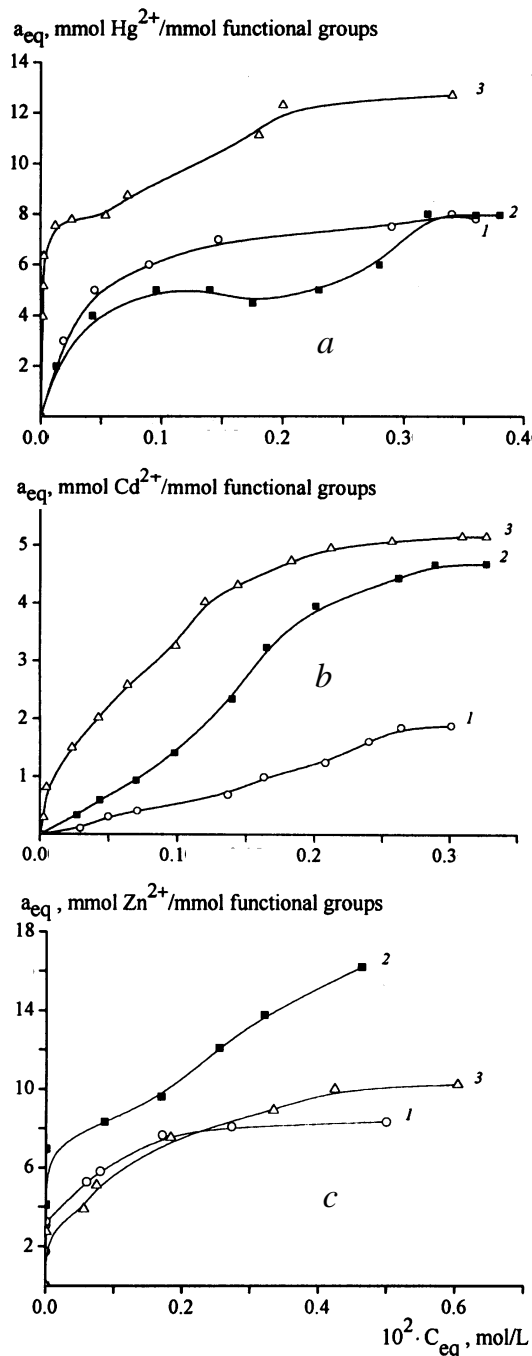

Fig. 8. Isotherms of mercury (II) (*a*), cadmium (II) (*b*) and zinc (II) (*c*) sorption on β-cyclodextrin-containing silicas.

T a b l e 4

Characteristic absorption bands of IR spectra (cm^{-1}) **for organosilicas before and after mercury (II), cadmium (II) and zinc (II) sorption**

Organosilica		Before sorption		After cation sorption
β-CD-1-SiO$_2$	3380, 1590	ν_{as}(N–H), δ(N–H) – primary amino groups	3380, 1525	ν_{as}(N–H), δ(N–H) – primary amino groups
	1490	δ(N–H) – secondary amino groups		
	3290	ν_s(O–H) – secondary alcohol groups of β-CD	3290	ν_s(O–H) – secondary alcohol groups of β-CD
	2950, 2880, 1460	ν_{as}(C–H), ν_s(C–H), δ(C–H) – methylene groups	2950, 1380	ν_{as}(C–H),δ(C–H) – methylene groups
β-CD-2-SiO$_2$	3380, 1540	ν_{as}(N–H), δ(N–H) – primary amino groups	3380, 1530	ν_{as}(N–H), δ(N–H) – primary amino groups
	1490	δ(N–H) – secondary amino groups	1490	δ(N–H) – secondary amino groups
	3290	ν_s(O–H) – secondary alcohol groups of β-CD		
	2965, 2880, 1455	ν_{as}(C–H), ν_s(C–H), δ(C–H) – methylene groups	2965, 2880	ν_{as}(C–H), ν_s(C–H) – methylene groups
	1755	ν(C=O) – bromoacetyl groups		
	680	ν(C–Br) – bromoacetyl groups		
β-CD-3-SiO$_2$	2970, 2880, 1455	ν_{as}(C–H), ν_s(C–H), δ(C–H) – methylene groups	2970, 2880	ν_{as}(C–H), ν_s(C–H) – methylene groups
	1540	δ(N–H) – primary amino groups	1520	δ(N–H) – primary amino groups
	1470	ν(–N–C–N–) – thiosemicarbazidoacetyl groups		
	1435	ν(C=S) – thiosemicarbazidoacetyl groups		

Sorption isotherms of mercury (II) on the synthesized β-CD-bonded silicas are well described by Langmuir equation (fig. 9) for monolayer adsorption on localized sites of energetically uniform surface [29] throughout the studied concentration range. For cadmium (II) the experimental data are well approximated in the coordinates of Freundlich equation (fig. 10) for sorption on heterogeneous surface [30]. The equilibrium sorption of Zn(II) onto β-CD-1-SiO$_2$ and β-CD-3-SiO$_2$ is well described by equation of Langmuir adsorption (fig. 11, *a*) and for β-CD-2-SiO$_2$ by Freundlich equation (fig. 11, *b*).

The "surface heterogeneity" of 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 Cd(NO$_3$)$^+$ ions simultaneously. Sorption of Zn^{2+} on β-CD-1-SiO$_2$ is described by Langmuir isotherm as organosilica contains the only type of sorption active centres — the secondary alcohol groups of chemically attached β-CD molecules (table 5). For β-CD-2-SiO$_2$ adsorption of zinc (II) is described by Freundlich equation, and "heterogeneous surface" is due to the presence of two types of sites (bromoacetyl and secondary alcohol groups) on the surface of this organosilica in which the rates of Zn(II) sorption, apparently, are essentially different. And finally, zinc (II) sorption on β-CD-3-SiO$_2$ is described by Langmuir isotherm. This indicates that the rate of sorption on the secondary alcohol and thiosemicarbazidoacetyl groups are almost identical.

β-CD-bonded silicas can be arranged in the following series with sorption capacity to mercury (II) and cadmium (II): β-CD-1-SiO$_2$ < β-CD-2-SiO$_2$ < β-CD-3-SiO$_2$, but for zinc (II): β-CD-1-SiO$_2$ < βCD-3-SiO$_2$ < β-CD-2-SiO$_2$. These results are consistent with those of the chemical and elemental analysis of supramolecular compounds formed on the organosilicas surface (table 6).

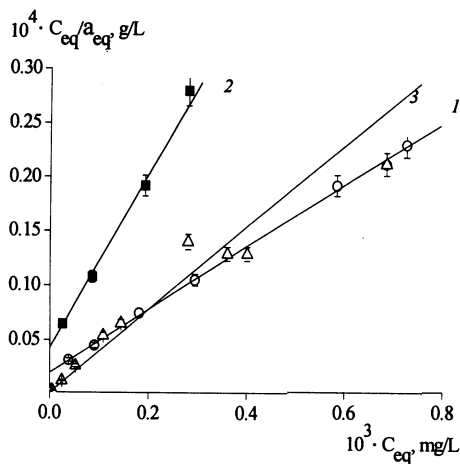β-Cyclodextrin has 14 side secondary alcohol

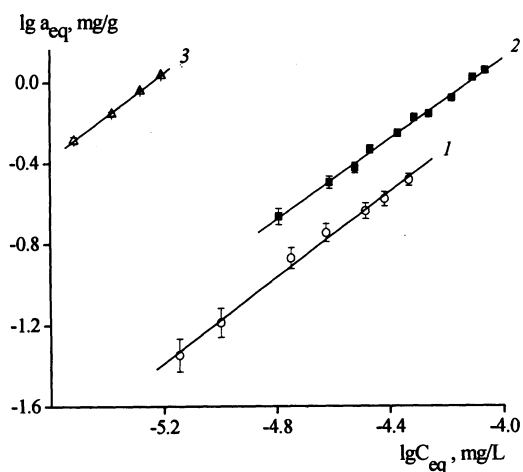Fig. 9. Isotherms of mercury (II) sorption on β-CD-1-SiO$_2$ —β-CD-3-SiO$_2$ (in coordinates of Langmuir equation).

Fig. 10. Isotherms of cadmium (II) sorption on β-CD-1-SiO2 —β-CD-3-SiO2 (in coordinates of Freundlich equation).

groups placed on the wide edge of its toroidal molecule [34]. The ratio [Hg(II)] : [β-CD] (table 6) reaching to 14 for β-CD-3-SiO$_2$ is proof that mercury cations sorption takes place not only on thiosemicarbazidoacetyl (or bromoacetyl) active centres, but also on residual secondary alcohol groups. The same goes for the sorption of cadmium cations. However, cadmium (II) is adsorbed much less mercury (II). The molar ratio [Cd(II)] : [β-CD] equals 1, 4 and 5, correspondingly. The ratio [Zn(II)] : [β-CD] (table 6) reaching to 14 for β-CD-2-SiO$_2$ is proof that zinc cations sorption takes place on residual secondary alcohol groups and bromoacetyl groups. The ratio of [Zn(II)] : [β-CD] = 10 for β-

CD-3-SiO$_2$ confirms participation in sorption not only secondary alcohols, but also thiosemicarbazidoacetyl groups. However, β-CD-2-SiO$_2$ has the highest sorption capacity with respect to zinc (II). These results can be explained in terms of the theory of hard and soft acids and bases.

According to the theory of hard and soft acids and bases [35—37], the cations of mercury and cadmium are "soft" acids, and Hg^{2+} is "softer" acid than Cd^{2+} [35]. Divalent cation of zinc is intermediate in a series of acids by Pearson theory. "Soft" acids form, as a rule, strong complexes with "soft" bases [35—37], whereas "hard" acids with "hard" bases. The centres of mercury (II), cadmium (II) and zinc (II) sorption on surface of synthesized organosilicas are grafted molecules of cyclic oligosaccharide which differ by chemical nature of side functional groups. The "softness" of side functional
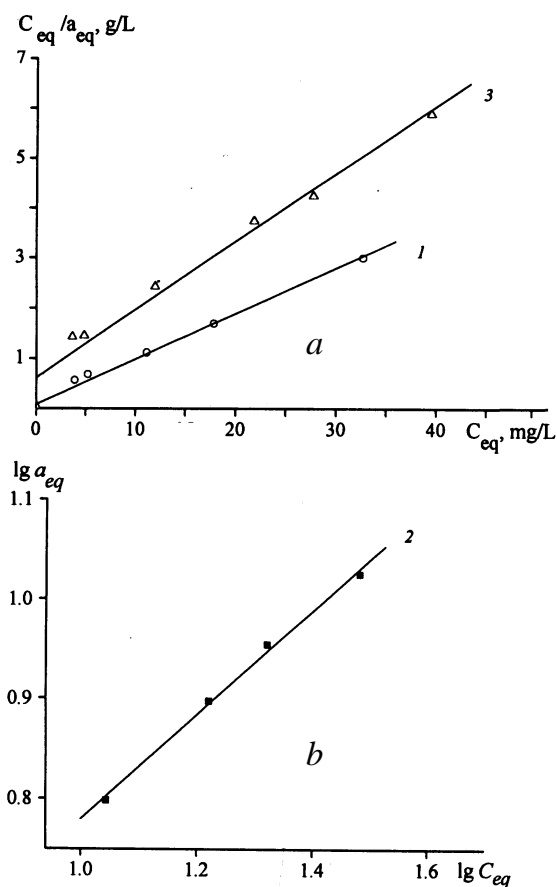

Fig. 11. Isotherms of zinc (II) sorption on β-CD-1-SiO$_2$ and β-CD-3-SiO$_2$ (a) and β-CD-2-SiO$_2$ (b) – lines 1, 3 and 2 – in coordinates of Langmuir and Freundlich equations, respectively.

T a b l e   5

Langmuir and Freundlich parameters for mercury (II), cadmium (II) and zinc (II) sorption on b-cyclodextrin-containing silicas

Ele-ments	Organosilica	Langmuir isotherm				Freundlich isotherm		
		a_m, mg/g	K_L, L/mg	R_L	R^2	K_F, mg/g	$1/n$	R^2
Hg(II)	β-CD-1-SiO$_2$	34 ± 2	14400 ± 700	0.65 ± 0.03	0.99			
	β-CD-2-SiO$_2$	12.6 ± 0.6	18800 ± 900	0.67 ± 0.03	0.99			
	β-CD-3-SiO$_2$	22 ± 1	330000 ± 10000	0.5 ± 0.2	0.99			
Cd(II)	β-CD-1-SiO$_2$					3.9 ± 0.2	0.80	0.99
	β-CD-2-SiO$_2$					4.3 ± 0.3	1.00	0.99
	β-CD-3-SiO$_2$					5.5 ± 0.3	1.25	0.99
Zn(II)	β-CD-1-SiO$_2$	0.22 ± 0.01	41 ± 2	0.24 ± 0.01	0.99			
	β-CD-2-SiO$_2$					4.0 ± 0.2	2.44	0.98
	β-CD-3-SiO$_2$	0.15 ± 0.01	11.2 ± 0.7	0.55 ± 0.03	0.99			

T a b l e   6

Chemical composition of surface supramolecular structures after sorption of mercury (II), cadmium (II) and zinc (II) nitrates on b-cyclodextrin-containing silicas

Organosilica	Hg(II)	Cd(II)	Zn(II)
β-CD-1-SiO$_2$	$C_{42}H_{70}O_{34} \cdot 5Hg(NO_3)_2$	$C_{42}H_{70}O_{34} \cdot Cd(NO_3)_2$	$C_{42}H_{70}O_{34} \cdot 7Zn(NO_3)_2$
β-CD-2-SiO$_2$	$C_{98}H_{112}O_{53}S_6Br_9 \cdot 8Hg(NO_3)_2$	$C_{98}H_{112}O_{53}S_6Br_9 \cdot 4Cd(NO_3)_2$	$C_{98}H_{112}O_{53}S_6Br_9 \cdot 14Zn(NO_3)_2$
β-CD-3-SiO$_2$	$C_{107}H_{148}O_{53}S_{15}N_{27} \cdot 14Hg(NO_3)_2$	$C_{107}H_{148}O_{53}S_{15}N_{27} \cdot 5Cd(NO_3)_2$	$C_{107}H_{148}O_{53}S_{15}N_{27} \cdot 10Zn(NO_3)_2$

groups of the wide edge of β-CDs increases in order: secondary alcohol < bromoacetyl < thiosemi-carbazidoacetyl groups. 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, while more "hard" cations of zinc (II) will form complexes preferably with the secondary alcohol groups and, possibly, with bromoacetyl groups. This is indeed observed in the experiment. From the theory of hard and soft acids and bases the contribution of inner cavity of β-CD molecules, occupied by "hard" nitrate-anion [36], to Hg(II), Cd(II) and Zn(II) sorption seems hardly probable. Nitrate-anion ("hard" base) forms strong inclusion complexes with β-CD cavity not only because of the geometric complementarity, but also to a large extent due to the presence of oxygen-containing fragments of "hard" acids in the glycosidic rings.

Most likely, the electroneutrality of inner cavity of β-CD, blocked by nitrate-anions, will be achieved by the interaction with "hard" acid, for example, with protons of nitric acid. Proton concentration in acidic solutions is significantly higher than that of mercury, cadmium or zinc cations.

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

Sorption of mercury (II), cadmium (II) and zinc (II) from aqueous solutions of corresponding nitrates has been studied. It has been proved that the equimolar nitrate-anions uptake takes place simultaneously with sorption of mercury, cadmium and zinc cations onto surface of organosilicas.

Active surface centres of β-CD-bonded silicas, which are responsible for Hg^{2+}, Cd^{2+}, $Cd(NO_3)^+$, Zn^{2+} and NO_3^- sorption, have been ascertained. The formation of surface supramolecular structures

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

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

The results obtained for the sorption of mercury (II), cadmium (II) and zinc (II) on the surface of nanoporous β-CD-bonded silicas with different functional substituents can predict its effectiveness for extraction from water, concentration and express-analysis of other metal ions, such as lead, chromium, arsenic, copper, nickel and cobalt.

РЕЗЮМЕ. Синтезовано нанопористі β-циклодекстринвмісні кремнеземи, які відрізняються функціональними замісниками широкого краю закріплених молекул циклічних олігосахаридів. Встановлено структуру та хімічний склад поверхні нанопористих органокремнеземів. Вивчено сорбцію ртуті (II), кадмію (II) та цинку (II) з розведених кислих нітратних розчинів нанопористими органокремнеземами. Результати сорбції проаналізовано з використанням кінетичної моделі Лагергрена та моделей рівноважної адсорбції Ленгмюра і Фрейндліха. Особливості взаємодії нітратів ртуті, кадмію та цинку з циклодекстринвмісними кремнеземами інтерпретовані з позицій теорії твердих і м'яких кислот та основ.

РЕЗЮМЕ. Синтезированы нанопористые β-циклодекстринсодержащие кремнеземы, отличающиеся функциональными заместителями широкого края химически привитых молекул циклических олигосахаридов. Установлена структура и химический состав поверхности нанопористых органокремнеземов. Изучена сорбция ртути (II), кадмия (II) и цинка (II) из разбавленных кислых нитратных растворов нанопористыми органокремнеземами. Результаты сорбции проанализированы с использованием кинетической модели Лагергрена и моделей равновесной адсорбции Ленгмюра и Фрейндлиха. Особенности взаимодействия нитратов ртути, кадмия и цинка с циклодекстринсодержащими кремнеземами интерпретированы с позиций теории твердых и мягких кислот и оснований.

REFERENCES

1. *Rath R.K., Subramanian S.* // Int. J. Miner. Process. -1999. -**57**, № 4. -P. 265—283.
2. *Ho Y.S., Porter J.F., McKay G.* // Water, Air and Soil Pollution. -2002. -**141**, № 1. -P. 1—33.
3. *Varma A.J., Deshpande S.V., Kennedy J.F.* // Carbohydrate Polymers. -2004. -**55**, № 1. -P. 77—93.
4. *Amphlett C.B.* Inorganic Ion Exchangers. -Amsterdam: Elsevier, 1964.
5. *Marhol M.* Ion Exchangers in Analytical Chemistry. Their Properties and Use in Inorganic Chemistry. -Prague: Academia, 1982.
6. *Ionites in Chemical Technology* / Eds. B.P.Nikol'skiy, P.G.Romankov. -Leningrad: Khimiya, 1982 (in Russian).
7. *Myasoedova G.V., Antokol'skaya I.I., Shoeva O.P. et al.* // Extraction and Ion Exchange. -1988. -**6**, № 2. -P. 301—321.
8. *Goncalves A.S., Alroldi C.* // Polyhedron. -1989. -**8**, № 24. -P. 2901—2906.
9. *Lehn J.M.* Supramolecular Chemistry. Concepts and Perspectives. -Weinheim-New York-Basel-Cambridge-Tokyo: VCH Verlagsgesellschaf, 1995.
10. *Qin L., He X.W., Li W.Y., Zhang Y.K.* // J. Chromatogr. A. -2008. -**1187**, № 1–2. -P. 94—102.
11. *Akiyama T., Hishiya T., Asanuma H., Komiyama M.* // J. Incl. Phenom. Macr. Chem. -2001. -**41**, № 1–4. -P. 149—153.
12. *Bibby A., Mercier L.* // Green Chem. -2003. -**5**, № 1. -P. 15—19.
13. *Iler R.K.* The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemistry of Silica. -New York: Wiley-Interscience, 1979.
14. *Tertykh V.A., Belyakova L.A.* Chemical Reactions with Participation of Silica Surface. -Kiev: Naukova Dumka, 1991 (in Russian).
15. *Vansant E.F., Van Der Voort P., Vrancken K.C.* Characterization and Chemical Modification on the Silica Surface. -Amsterdam: Elsevier, 1995.
16. *Steed J.W., Atwood J.L.* Supramolecular Chemistry. -New-York: John Wiley and Sons, 2000.
17. *Shiraishi S., Komiyama M., Hiray H.* // Bull. Chem. Soc. Jap. -1986. -**59**, № 2. -P. 507—511.
18. *Kawaguchi Y., Tanaka M., Nakae M. et al.* // Anal. Chem. -1983. -**55**, № 12. -P. 1852—1857.
19. *Ng S.C., Ong T.T., Fu P., Ching C.B.* // J. Chromatogr. A. -2002. -**968**, № 1–2. -P. 31—40.
20. *Glennon J.D., O'Connor K., Srijaranai S.I. et al.* // Anal.Proc. -1993. -**26**. -P. 153—159.
21. *Hu W., Li J.S., Feng Y.Q. et al.* // Chromatographia. -1998. -**48**, № 3/4. -P. 245—250.
22. *Jal P.K., Patel S., Mishra B.K.* // Talanta. -2004. -**62**, № 5. -P. 1005—1028.
23. *Phan T.N.T., Bacquet M., Morcellet M.* // React. Funct. Polym. -2002. -**52**. -P. 117—125.
24. *Belyakova L.A., Kazdobin K.A., Belyakov V.N. et al.*

// J. Colloid Interf. Sci. -2005. -**283**, № 1–2. -P. 488—494.

25. *Belyakova L.A., Varvarin A.M., Lyashenko D.Yu., Khora O.V.* // Ads. Sci. Technol. -2005. -**23**, № 9. -P. 703—719.

26. *Schwarzenbach G., Flashka H.* Die Komplexonometrische Titration. -Stuttgard: Ferdinant Enke,Verlag, 1965.

27. *Studlar K., Janousek I.* // Talanta. -1961. -**8**, № 4. -P. 203—208.

28. *Gupta S.S., Bhattacharyya K.G.* // J. Colloid Interf. Sci. -2006. -**295**, № 1. -P. 21—32.

29. *Langmuir I.* // J. Amer. Chem. Soc. -1918. -**40**, № 9. -P. 1361—1403.

30. *Freundlich H., Heller W.J.* // Ibid. -1939. -**61**, № 8. -P. 2228—2230.

31. *Gao X.M, Tong L.H., Inoue Y., Tai A.* // Synthetic Communications. -1995. -**25**, № 5. -P. 703—710.

32. *Rao C.N.R.* Ultra-Violet and Visible Spectroscopy, Chemical Applications. -London: Butterworth, 1961.

33. *Wen X., Tan F., Jing Z., Liu Z.* // J. Pharm. Biomed. Analysis. -2004. -**34**, № 3. -P. 517—523.

34. *Szejtli J.* // Chem. Rev. -1998. -**98**, № 5. -P. 1743—1752.

35. *Pearson R.G.* // J. Chem. Educ. -1968. -**45**, № 10. -P. 643—648.

36. *Pearson R.G.* // J. Amer. Chem. Soc. -1963. -**85**, № 22. -P. 3533—3539.

37. *Pearson R.G.* // J. Chem. Sci. -2005. -**117**, № 5. -P. 369—377.

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