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ADSORPTION AND COMPLEXING PROPERTIES OF SILICA MODIFIED WITH β-CYCLODEXTRIN

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The sorption of cadmium (II) cations on the surface of amorphous macroporous silicas chemically modified with β-cyclodextrin and its functional derivatives has been studied. It was shown that sorption of cadmium (II) follows the Frendlich isotherm for heterogeneous surface. Analysis of sorption kinetic curves in the framework of the Lagergren kinetic model for reactions of pseudo-first and pseudo-second order shows that two parallel processes take place on the surface of β-cyclodextrin-containing silicas. It has been proved that significant increasing of cadmium (II) nitrate sorption is a result of uncharged supramolecular structures formation on the surface of silicas modified with β-cyclodextrins. The chemical composition of these supramolecular structures correlates with the polarizability of functional substituents of β-cyclodextrins.

INTRODUCTION

Chemical immobilization of macrocyclic organic compounds capable to form inclusion complexes of "host–guest" type with ions and molecules on the surface of oxide materials is a promising method for the design of active sites of extraction and concentration of impurities of toxic substances, and also for their chemical analysis in water and other objects of environment [1–6]. Among oxide materials highly disperse amorphous silicas possess undoubted advantages due to not only chemical, hydrolytic, thermal, and radiation resistances, but also in-depth studied structure and reactivity of its surface active centers [7–11].

The purpose of this work is to study the influence of the surface structure of β-cyclodextrin-containing silicas on Cd (II) ions sorption from weakly acidic solutions.

EXPERIMENTAL

Highly disperse amorphous macroporous silica– Silochrome C-120 with specific surface area of 118 $m^2\ g^{-1}$, average pore diameter of 40 nm, and silanol groups concentration of 0.4 mmol g^{-1} was used as an initial silica adsorbent and support in the synthesis of organosilicas.

Chemical immobilization of β-cyclodextrins was made on the surface of Silochrome C-120 through multi-step chemical modification (Fig. 1).

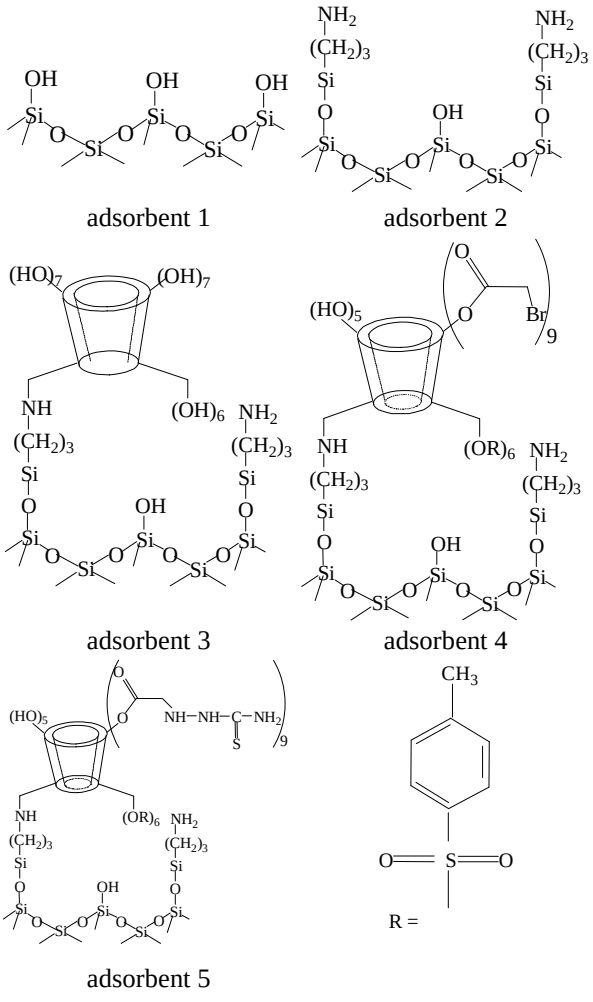

Fig. 1. Surface structure of synthesized silica adsorbents

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Aminopropylsilica (adsorbent 2) was obtained by interaction of hydroxylated silica (adsorbent 1) with γ-aminopropyltriethoxysilane. Organosilicas chemically modified with β-cyclodextrin were synthesized by interaction of aminopropylsilica with mono-toluenesulfonyl-β-CD (adsorbent 3); bromine derivative of heptakis-(toluenesulfonyl)-β-CD with aminopropylsilica (adsorbent 4) and chemical interaction of bromoacetyl groups of adsorbent 4 with thiosemicarbazide (adsorbent 5).

Structural and sorption parameters, chemical composition and structure of the surface layer of silica adsorbents (Table 1) were determined from the isotherms of low-temperature nitrogen adsorption, elemental and chemical analysis, potentiometric titration, thermogravimetry data, IR, UV, and ^{1}H NMR spectroscopy.

Table 1. Chemical composition of surface layer of synthesized silica adsorbents

Adsorbent	Concentration of functional groups of adsorbent, mmol g^{-1}	Content of chemical elements, %				
		H	C	N	S	Br
1	0.40	–	–	–	–	–
2	0.28	0.45	1.00	0.40	–	–
3	0.035	0.70	2.80	0.40	–	–
4	0.01	0.60	2.20	0.40	0.20	0.70
5	0.01	0.65	2.30	0.80	0.50	–

Sorption of Cd (II) ions was studied at 22°C under static conditions using multi-batch method from $2.5\cdot10^{-4}$ to $4.0\cdot10^{-3}$ M (pH ~ 1) $Cd(NO_3)_2$ aqueous solutions as a function of contact time with silica and the equilibrium solution concentration. Suspensions containing 0.025 g of silica adsorbent and 20 cm^3 of $Cd(NO_3)_2$ solution were kept for 4 h in a JULABO SW22 water thermostat with continuous shaking (shaking frequency 110 rpm). The amount of Cd (II) ions in the initial and equilibrium solutions was determined by the absorption band with λ_{max}= 576 nm using xylenol orange as reagent on a Perkin Elmer Lambda 35 spectrophotometer.

The relative content of various cadmium (II) species in aqueous solutions at pH 1–5 depending on the concentration of free NO_3^- ions was calculated using the program Chemical Equilibria in Aquatic System.

Ultraviolet absorption spectra of $Cd(NO_3)_2$ aqueous solutions were recorded on a Specord M-40 spectrophotometer in the wavelength range 240–400 nm in quartz cells with l = 1 cm.

Infrared transmission spectra were registered in the frequency range 4000–400 cm^{-1} using a Thermo Nicolet NEXUS FT-IR spectrophotometer. To record the IR spectra samples of adsorbents of ~30 mg each were compacted in plates under the pressure of 10^8 Pa.

RESULTS AND DISCUSSION

From aqueous solutions of cadmium nitrate with pH ~ 1 Cd (II) ions can be adsorbed on the surface of studied silicas as two existing species: Cd^{2+} and $Cd(NO_3)^+$, 80% of which being divalent cation. Sorption equilibrium is achieved within 1 h, and for organosilicas 3–5 substantial sorption capacity is already realized in the first 15 minutes (Fig. 2). The isotherms of Cd (II) ions sorption for all studied functional silicas are presented in Fig. 3.

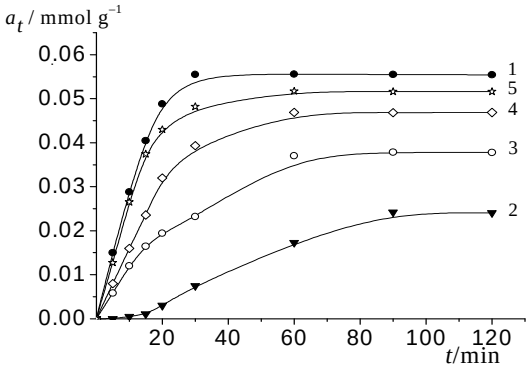

Fig. 2. Effect of agitation time on sorption of Cd (II) ions by silica adsorbents 1–5 (10^{-3} M cadmium (II) nitrate aqueous solution)

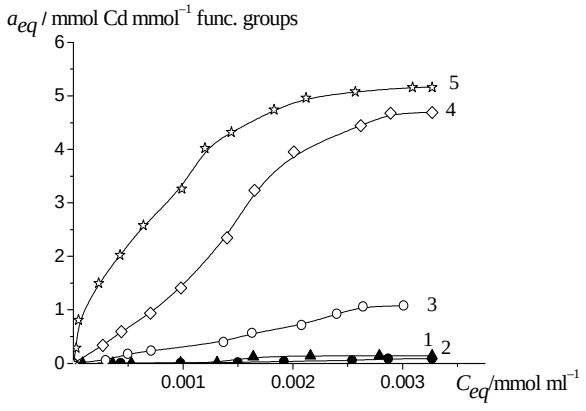

Fig. 3. Isotherms of Cd (II) cations sorption for silica adsorbents 1–5

Adsorbents 1 and 2 practically do not absorb cations Cd (II) from solutions with a concentration less than 0.001 M. The maximum sorption of Cd (II) from 0.001 M aqueous solutions over the content of chemically grafted β-*CD* at 1.1, 1.6, and 5.2 times for adsorbents 3–5, respectively, and the distribution coefficients increase by two orders of magnitude in comparison with that of initial silica (Table 2).

Table 2. Structural and sorption parameters of silica adsorbents

Adsorbent	Specific surface area, $m^2\ g^{-1}$	Specific sorption of Cd (II) cations, %	Distribution coefficient, $L\ g^{-1}$
1	118	14	7
2	111	9	5
3	98	110	125
4	90	460	200
5	85	520	340

The IR spectrum of silica 1 after adsorption of cadmium (II) is practically unchanged. In the IR spectrum of adsorbent 2 a little shift of the absorption band of the deformation vibrations of the N–H bond in the primary amino groups (1571 and 1542 cm^{-1}) into low-frequency range (1520 cm^{-1}) is observed, indicating the formation of a complex between aminopropyl groups and Cd (II) ions [12]. In the IR spectrum of adsorbent 3, besides the absorption bands belonging to the aminopropyl groups, the absorption bands of the valence vibrations of the O–H bond for secondary alcohol groups (3375, 3290 cm^{-1}) of β-CD are present. At the same time, the intensity of the valence and deformation vibrations of the C–H bonds (2950, 2880 cm^{-1} and 1460, 1390 cm^{-1} respectively) is higher than that for silica 2. After adsorption of cadmium (II) the absorption bands of the valence vibrations of β-CD become less pronounced, and the absorption bands of the deformation vibrations of the N–H and C–H bonds are shifted into low-frequency region (1525, 1400, and 1325 cm^{-1}). In the IR spectrum of adsorbent 4 the absorption bands of heptakis-(toluenesulfonyl)-β-CD, namely, the bands of the deformation vibrations of the O–H bond in the COH groups (1365 cm^{-1}), the valence vibrations of the C=C bond in the benzene ring of toluenesulfonyl groups (1490 cm^{-1}), the characteristic absorption bands of the valence vibrations of the C=O (1755 cm^{-1}) and C–Br bonds (680 cm^{-1}) of the bromoacetyl groups have been registered. The absorption band at 1455 cm^{-1} belongs to the deformation vibrations of the C–H bond, the absorption bands at 1560 and 1540 cm^{-1} were attributed to the deformation vibrations of the N–H bonds in the amino groups. After adsorption of cadmium (II) the absorption bands of the valence vibrations of the C–H bonds become less clear, the characteristic absorption bands of the C–Br and C=O bonds of the bromoacetyl groups are absent; the absorption bands of the deformation vibrations of the N–H bond are shifted in low-frequency region (1530 cm^{-1}). In the IR spectrum of adsorbent 5 the absorption bands of the valence vibrations of the C–H bond (2970, 2935, 2880 cm^{-1}) of the methylene groups and the deformation vibrations of the O–H bond (1635 cm^{-1}) of the COH groups are observed. The absorption band at 1540 cm^{-1} corresponds to the deformation vibrations of the N–H bond in the amino groups, the absorption bands at 1470 and 1435 cm^{-1} were attributed to the deformation vibrations of the amino groups and the valence vibrations of the N–C–N and C=S bonds in thiosemicarbazide groups. After adsorption of cadmium (II) the absorption bands of the valence vibrations of the N-C–N and C=S bonds disappear, and the absorption band of the deformation vibrations of the amino groups is shifted in low-frequency region (1520 cm^{-1}). Hence, the side functional groups of the upper (wider) edge of β-CD molecule and its derivatives fixed on the surface of macroporous amorphous silica participate in the complex formation with Cd (II) ions. Increase of sorption affinity in the series adsorbent 3 < adsorbent 4 < adsorbent 5 correlates with chelating ligands ability [13].

The interaction of β-cyclodextrin with cadmium (II) nitrate in a solution was studied to clarify the role of the inner cavity of β-cyclodextrin in the sorption of cadmium on organosilicas. The electronic spectrum of cadmium (II) nitrate solution contains a symmetric absorption band with λ_{max} = 301 nm and ε = 710 L mol^{-1} cm^{-1} which is assigned to $n \rightarrow \pi^*$ transition of the N=O chromophore in nitrate-ion [14]. Upon the addition of certain amounts of β-CD to a $Cd(NO_3)_2$ solution, the absorption band at 301 nm becomes asymmetric and increases sharply in intensity (ε = 4000 L mol^{-1} cm^{-1}). Since β-CD does not have characteristic absorption bands in the UV region, such spectral changes of the absorp-

tion band of chromophore N=O show the interaction of NO_3^- ions with β-CD, namely, the formation of inclusion complex of "host–guest" type.

Composition of inclusion compound was determined by equimolar series method. The experimental data plotted in coordinates of the Benesi-Hildebrand equation [15] fall on a straight line for the complex of 1:1 (Fig. 4)

$$(C^o_{NO_3^-} \cdot l) / D^\lambda = 1 / \varepsilon^\lambda + 1 / (K_s \cdot \varepsilon^\lambda \cdot C^o_{\beta\text{-CD}}),$$

where C^o is initial concentration of reagents (mol L^{-1}); D^λ is optical density of equilibrium solutions, arbitrary units (arb. u.); ε^λ is molar extinction coefficient of equilibrium solutions (L mol^{-1} cm^{-1}); K_s is stability constant of the complex (L mol^{-1}); l is thickness of absorbing layer of analyzed solution (cm).

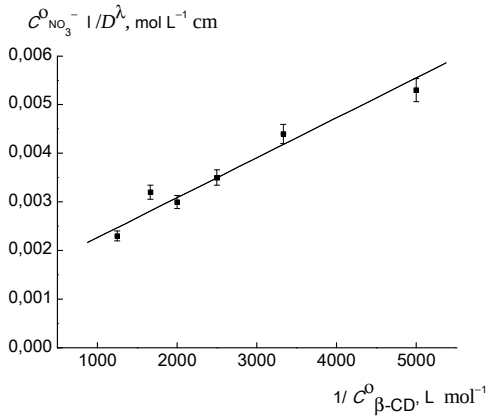

Fig. 4. Dependence of spectral characteristics of NO_3^- on amount of β-CD in aqueous solutions in coordinates of the Benesi–Hildebrand equation for inclusion compound of composition 1:1

The volume of inner cavity of β-CD molecule is $V_{\text{cavity }\beta\text{-CD}} = 0.262$ nm^3; its upper part is $V_{½\text{ cavity }\beta\text{-CD}} = 0.156$ nm^3, the volume and diameter of hydrated nitrate-ion are $V_{NO_3^-} = 0.153$ nm^3 and $d_{NO_3^-} = 0.67$ nm, respectively [16]. Consequently, the entry of the anion into the inner cavity of β-*CD* is possible only through a wider edge, and location of NO_3^- – in the top of β-CD torus. The stability constant of complex "β-CD – NO_3^-" is $K_s = 1425 \pm 70$ L mol^{-1}. The reason for high strength of formed inclusion complex is that the volumes of hydrated anion and upper part of inner cavity of β-CD are virtually identical.

It has been found using chemical analysis that the interaction product of β-CD (or its bromine- and sulfur-containing derivatives) with $Cd(NO_3)_2$ contains not only nitrate-ions, but also Cd^{2+} in the ratio $[NO_3^-]:[Cd^{2+}] = 2:1$. Hence, for β-CD-containing silicas the molecular sorption of cadmium nitrate is observed. Chemical composition of formed surface supramolecular compounds is given in Table 3.

Table 3. Chemical composition of surface supramolecular structures

Adsorbent	Functional groups of β-cyclodextrins		Chemical composition of supra–molecular structures (elemental analysis)
	type	quantity	
3	alcohol	21	$C_{42}H_{70}O_{34} \cdot Cd(NO_3)_2$
4	bromoacetyl	9	$C_{98}H_{112}O_{53}S_6Br_9 \cdot 4\ Cd(NO_3)_2$
5	thiosemicarbazide	9	$C_{107}H_{148}O_{53}S_{15}N_{27} \cdot 5\ Cd(NO_3)_2$

The isotherms of cadmium (II) sorption for adsorbents 3–5 were expressed in the coordinates of the Freundlich and Langmuir equations [17, 18]. The experimental data are well fitted to linear form of the Freundlich equation for adsorption on heterogeneous surface (Fig. 5)

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

where a_{eq} is equilibrium sorption (mg g^{-1}); K_F is the Freundlich constant, sorption capacity (mg g^{-1}); $1 / n$ is the Freundlich constant which characterizes the sorption intensity; C_{eq} is adsorbate equilibrium concentration in a solution (mg L^{-1}).

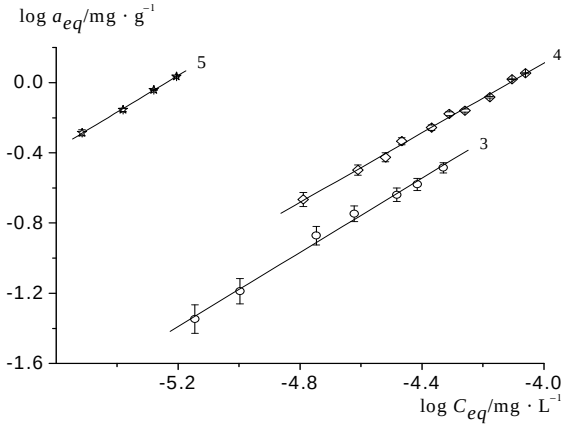

Fig. 5. Isotherms of Cd (II) cations sorption in the Freundlich equation for adsorbents 3–5

The calculated Freundlich constants are given in Table 4. The increase of the constants K_F and n in order adsorbent 3 < adsorbent 4 < adsorbent 5 is an evidence of rising contribution of side functional groups of immobilized β-cyclodextrins to

Cd^{2+} sorption. Thus, the surface heterogeneity of adsorbents 3–5 may be due to the presence of two types of centers for sorption of Cd (II) – the inner cavity of immobilized β-CD molecules and the side alcohol, bromoacetyl, and thiosemicarbazide groups (Fig. 1). It should be taken into account that both Cd^{2+} and $Cd(NO_3)^+$ ions can be adsorbed.

Table 4. Freundlich isotherm constants n and K_F for cadmium (II) cations sorption by β-cyclodextrin-containing silicas at 22°C

Adsorbent	n	K_F, mg · g^{-1}	R^2
3	0.80	3.90± 0.23	0.99
4	1.00	4.30 ± 0.26	0.99
5	1.25	5.50 ± 0.33	0.99

The Lagergren kinetic models [19] for processes of pseudo-first order

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

where a_t and a_{eq} are sorption (mg g^{-1}) at time t and at equilibrium, respectively (min), k_1 is rate constant of sorption (min^{-1}),
and pseudo-second order

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

where k_2 is rate constant of sorption (g·mg^{-1}·min^{-1}), were used for analysis of the kinetic curves of Cd (II) sorption. The kinetic curve (Fig. 6) for adsorbent 3 is linear in the coordinates of the equation for the processes of pseudo-second order (the rate constant of sorption $k_2 = 0.312 \pm 0.019$ g·mg^{-1}·min^{-1}, the correlation coefficient $R^2 = 0.99$).

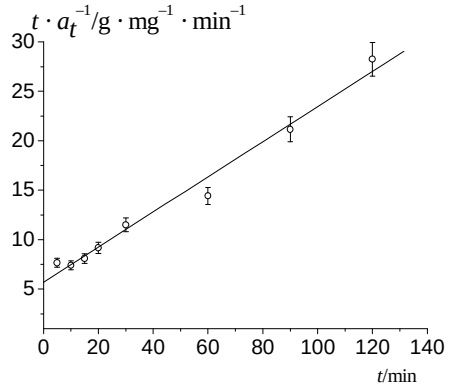

Fig. 6. Kinetic curve of Cd (II) cations sorption in the Lagergren pseudo-second order equation for adsorbent 3

It can be explained by the passing of two parallel reactions with substantially various rates on the surface of adsorbent 3. This is the interaction of cadmium cations with inner cavity of chemically fixed β-CD molecules and its side alcohol groups. This explanation seems to be quite reasonable, since the amount of adsorbed cadmium (II) slightly exceeds the content of grafted β-CD (Table 2, 3). In other words, Cd (II) sorption occurs mainly with participation of inner cavity of β-CD.

Kinetic curves for adsorbents 4 and 5 (Fig. 7) correspond to the model of the processes of pseudo-first order ($R^2 = 0.99$ and $k_1 = 1.88 \pm 0.11$ and 1.97 ± 0.12 min^{-1}, respectively).

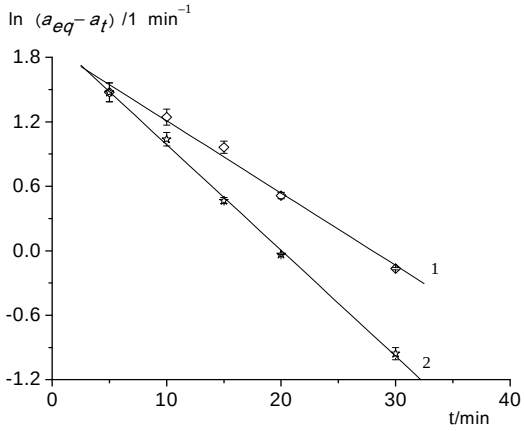

Fig. 7. Kinetic curves of Cd (II) cations sorption in the Lagergren pseudo-first order equation for adsorbents 4 (*1*) and 5 (*2*)

It agrees well with substantial increasing of the complex formation ability of the bromoacetyl and thiosemicarbazide substituents in comparison with alcohol groups [20] (Table 3). Typical changes of IR spectra of adsorbents 1–5 after cadmium (II) sorption confirm this conclusion. Thus, the cadmium cations interact with side functional groups of β-cyclodextrin chemically grafted on the silica surface, and also with inner cavity of β-CD (through NO_3^-) forming uncharged supramolecular structures on the surface of silica adsorbents. Chemical composition of these supramolecular structures correlates with polarizability of side groups of β-CD.

CONCLUSIONS

Interaction of $Cd(NO_3)_2$ with β-CD in a solution and on the surface of highly disperse amorphous silicas chemically modified with β-cyclo-

dextrin or its bromine- and sulfur-containing functional derivatives has been studied by use of IR and UV spectroscopy, elemental and chemical analysis, and also adsorption measurements. It has been shown that sorption of Cd (II) follows the Freundlich isotherm for heterogeneous surface. Analysis of sorption kinetic curves in the framework of the Lagergren kinetic model for the processes of pseudo-first and pseudo-second order confirms that two parallel processes take place on the surface of β-cyclodextrin-containing silicas. It has been proved that molecular sorption of $Cd(NO_3)_2$ is attended with the formation of supramolecular structures on the surface of β-CD-containing silicas. Chemical composition of these structures correlates with polarizability of functional groups of β-cyclodextrins.

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Адсорбційні та комплексоутворюючі властивості кремнезема, модифікованого β-циклодекстрином

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Вивчено сорбцію катіонів кадмію (II) на поверхні аморфних макропористих кремнеземів, хімічно модифікованих β-циклодекстрином та його функціональними похідними. Показано, що сорбція кадмію (II) відповідає ізотермі Фрейндліха для гетерогенної поверхні. Аналіз кінетичних кривих сорбції у рамках кінетичної моделі Лагергрена для реакцій псевдопершого і псевдодругого порядку показує, що на поверхні β-циклодекстринвмісних кремнеземів відбувається два паралельні процеси. Доведено, що істотне збільшення сорбції нітрату кадмію (II) є результатом формування незаряджених супрамолекулярних структур на поверхні кремнеземів, модифікованих β-циклодекстринами. Хімічний склад цих супрамолекулярних структур корелює з поляризацією функціональних замісників β-циклодекстринів.

Адсорбционные и комплексообразующие свойства кремнезема, модифицированного β-циклодекстрином

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Изучена сорбция катионов кадмия (II) на поверхности аморфных макропористых кремнеземов, химически модифицированных β-циклодекстрином и его функциональными производными. Показано, что сорбция кадмия (II) соответствует изотерме Фрейндлиха для гетерогенной поверхности. Анализ кинетических кривых сорбции в рамках кинетической модели Лагергрена для реакций псевдопервого и псевдовторого порядка показывает, что на поверхности β-циклодекстринсодержащих кремнеземов осуществляется два параллельных процесса. Доказано, что существенное увеличение сорбции нитрата кадмия (II) является результатом образования незаряженных супрамолекулярных структур на поверхности кремнеземов, модифицированных β-циклодекстринами. Химический состав этих супрамолекулярных структур коррелирует с поляризуемостью функциональных заместителей β-циклодекстринов.