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Silica Modified with Bromine Derivative of Heptakis-(6-O-(Toluenesulfonyl))- β -Cyclodextrin: Synthesis, Structure and Adsorption Properties

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Multistep chemical modification of silica surface with bromine derivative of heptakis-(6-O-(toluenesulfonyl))- β -cyclodextrin has been realized. IR spectroscopy and quantitative chemical analysis of surface compounds were used to prove surface structure of modified silica. It has been studied adsorption of Hg (II) ions from diluted aqueous solutions. It has been determined considerable increasing of silica adsorption affinity to mercury ions due to the formation of supramolecular structures with chemically immobilized bromine derivative of heptakis-(6-O-(toluenesulfonyl))- β -cyclodextrin on its surface.

Key words: silica surface, β -cyclodextrin, immobilization, mercury (II) nitrate, adsorption.

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Introduction

Great interest to cyclodextrins (cyclic oligosaccharides) is caused by their unique ability to form inclusion complexes of the "host-guest" type with many organic compounds [1,2]. Cyclodextrins (CDs) can be used as materials for creation of selective adsorbents, active catalysts and sensors [3-5], chromatographic separation and purification of organic compounds of similar structure and composition [6], extraction and concentration of impurities of toxic substances [7]. The study of adsorptive specificity of CDs with respect to heavy metals ions for their chemical analysis, removal from the environment and utilization [8] is of profound importance. In [7,9,10], for example, experimental results of β -CD interaction with Cu (II), Pb (II), Cd (II) ions are presented. Nevertheless, systematic investigations of CDs complex formation capability with metal ions are not available.

Insoluble CDs are most suitable for practical application. Therefore, much attention is given to production of modified water-insoluble cyclic oligosaccharides, CDs' conversion into insoluble state by means of synthesis of cyclodextrin-containing materials via impregnation and polymerization of appropriate monomers [1,2,11]. Chemical immobilization on a surface of inorganic supports can be used as alternative way to get insoluble cyclodextrins. Geometrical and structure uniformity of surface active sites, high rate of

achievement of adsorption equilibrium are among advantages of chemical attachment of CDs to a surface of highly dispersed nonporous and wide-porous inorganic supports.

In this work an influence of chemical immobilization of bromine derivative of heptakis-(6-O-(toluenesulfonyl))- β -cyclodextrin (Br-Ts- β -CD) on adsorption ability of amorphous wide-porous silica towards Hg (II) ions has been studied. Mercury compounds have high toxicity. Thus, creation of novel adsorbents for quantitative express-analysis of Hg (II) impurities in water and food-stuffs as well as for its effective concentration and extraction from diluted aqueous solutions is of significant importance.

I. Experimental

The macroporous silica Silochrome (C-120) with specific surface area of 118 m²/g, average pore diameter of 40 nm, and the concentration of silanol groups of 0,4 mmol/g was used as starting silica adsorbent.

β -cyclodextrin (99% purity) from Fluka, 4-toluenesulfonyl chloride ($\geq 98\%$ purity) and bromoacetyl bromide ($\geq 98\%$ purity) from Merck, mercury nitrate (AnalaR grade) from Khimlaborreaktiv were used without additional purification.

Infrared spectra were registered in the range from 4000 to 400 cm⁻¹ using Thermo Nicolet NEXUS FT-IR spectrophotometer. To record IR spectra, adsorbents

were pressed under pressure of 10^8 Pa in plates (~30 mg).

Elemental analysis was performed with use of Elemental Analyzer EA 1110.

The concentration of silanol groups of studied adsorbents was determined by chemisorption of dimethylchlorosilane. Aminopropyl groups amount was estimated with potentiometric titration and thermal gravimetric analysis. The latter method was used for determination of immobilized β -cyclodextrin content [12].

Adsorption of Hg (II) ions on silicas from $2,5 \cdot 10^{-4}$ to $4,0 \cdot 10^{-3}$ M aqueous solutions of mercury nitrate was studied by multibatch method depending on duration of contact with adsorbents and concentration of equilibrium solution under static conditions at 22°C. The amount of Hg (II) ions in initial and equilibrium solutions was tested by atomic absorption spectrometry using Pye Unicam SP-9 equipment and with trilonometric back titration [13].

II. Results and discussion

The chemical immobilization of bromine derivative of heptakis-(6-*O*-(toluenesulfonyl))- β -cyclodextrin on silica surface was carried out in two steps. It included the interaction of starting silica with γ -aminopropyltriethoxysilane and then with Br-Ts- β -CD.

The synthesis of bromine derivative of heptakis-(6-*O*-(toluenesulfonyl))- β -cyclodextrin requires the obtaining of heptakis-(6-*O*-(toluenesulfonyl))- β -cyclodextrin and its interaction with bromoacetyl bromide [14]:

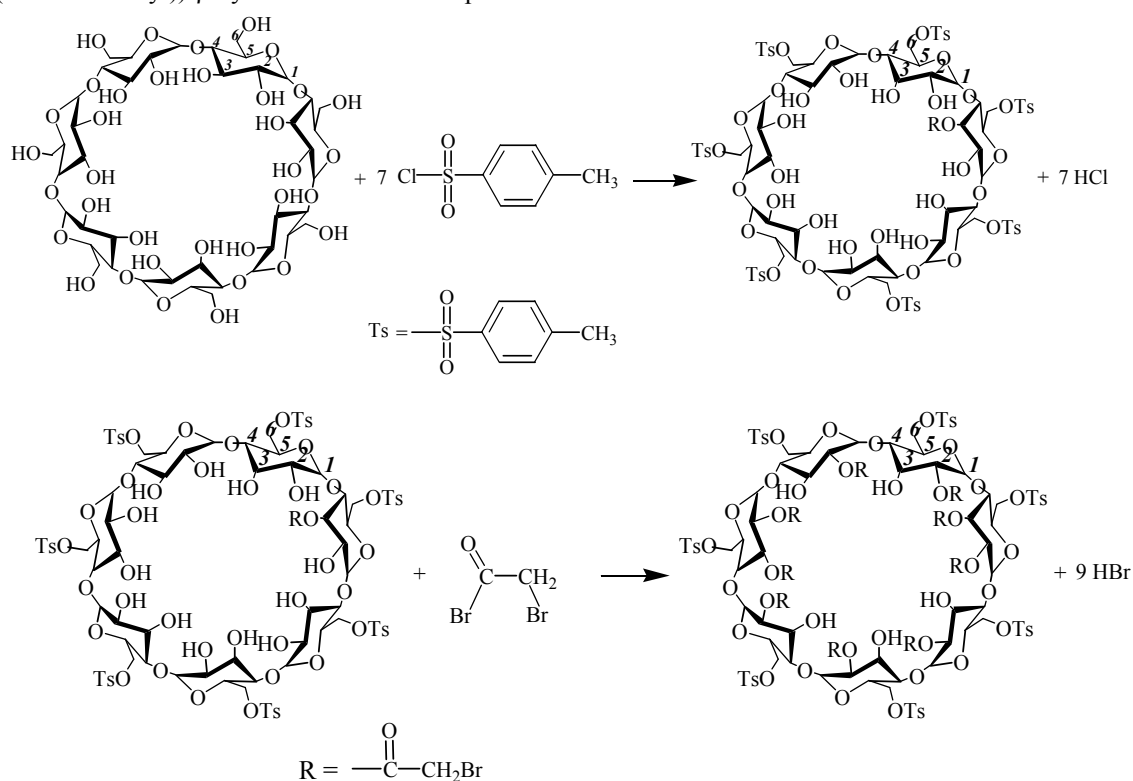
Based on the data of elemental analysis (Table 1) it is believed that all the secondary OH-groups of heptakis-(6-*O*-(toluenesulfonyl))- β -cyclodextrin at the 2-position

and two hydroxyl groups at the 3-position have taken part in the chemical reaction with bromoacetyl bromide [1]:

Modification of silica surface with aminopropyl groups was carried out according to the procedure described in [15]. Interaction of aminopropylsilica with the bromine derivative of heptakis-(6-*O*-(toluenesulfonyl))- β -cyclodextrin has been realized under conditions of optimal running of the reaction of electrophilic substitution of proton in aminopropyl groups with β -cyclodextrin ones [12]. The grafting of Br-Ts- β -CD takes place predominantly by tosyl groups as demonstrated by the results of elemental analysis (Table 2).

In the IR spectrum of aminopropylsilica (Fig. 1c, Table 2, adsorbent 2) the characteristic absorption bands at 3377, 3307 and 1571 cm^{-1} belonging to the valence and the deformation vibrations of the N-H bond in the grafted amino groups and the absorption bands at 2954, 2929, 2880 and 1458, 1413 cm^{-1} corresponding to the valence and the deformation vibrations of the C-H bonds in the hydrocarbon groups are registered [16, 17].

In the IR spectrum of bromine derivative of heptakis-(6-*O*-(toluenesulfonyl))- β -cyclodextrin (Fig. 2a) there are the following absorption bands: at 3375 cm^{-1} , the band of the valence vibrations of the O-H bond in the secondary hydroxyl groups of Br-Ts- β -CD connected by hydrogen bonds [1]; at 2940 cm^{-1} , the band of the valence vibrations of the C-H bond in the methylene groups; at 1755 cm^{-1} , the band of the valence vibrations of the C=O bond in the bromoacetyl groups; at 1635 cm^{-1} , the band of the deformation vibrations of the O-H bonds in the COH groups and / or in the water molecules; at 1610 and 1495 cm^{-1} , the bands of the valence vibrations of the C=C bond in the benzene ring of the tosyl groups; at 1425 and 1290 cm^{-1} , the bands of the deformation



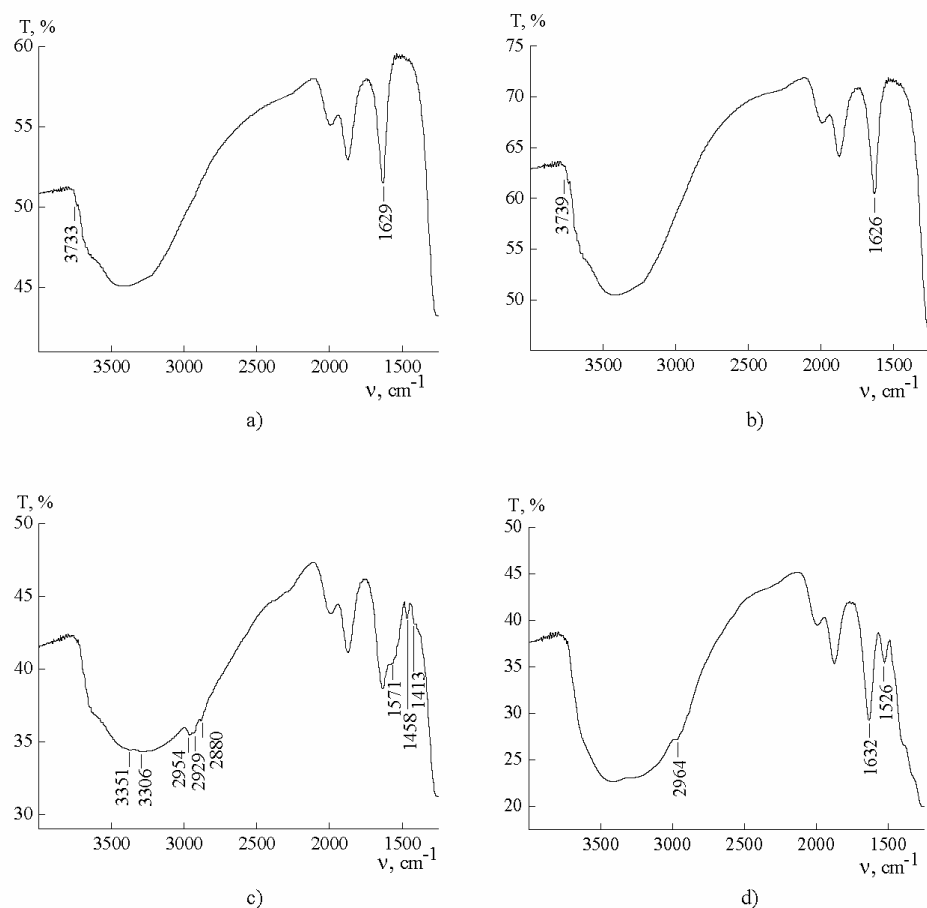


Fig. 1. IR spectra for adsorbents 1 and 2 before (a, c) and after (b, d) adsorption of mercury (II) ions.

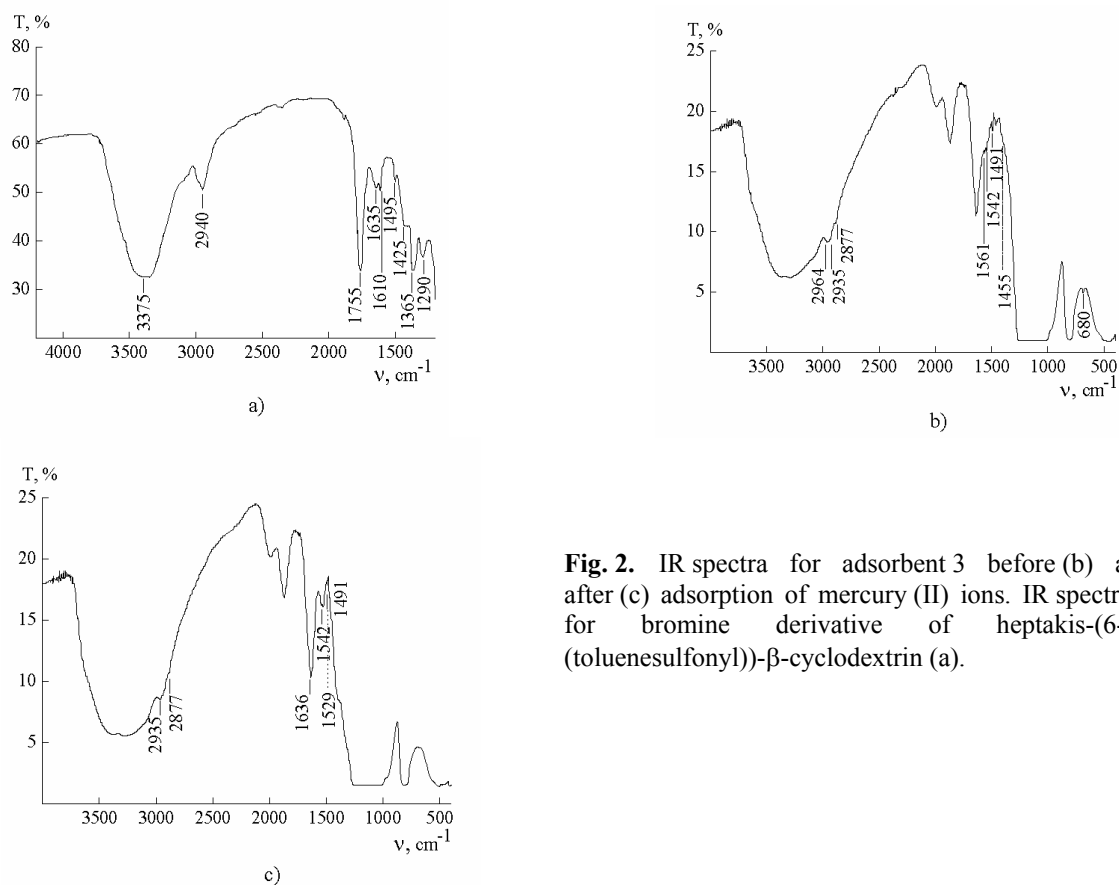
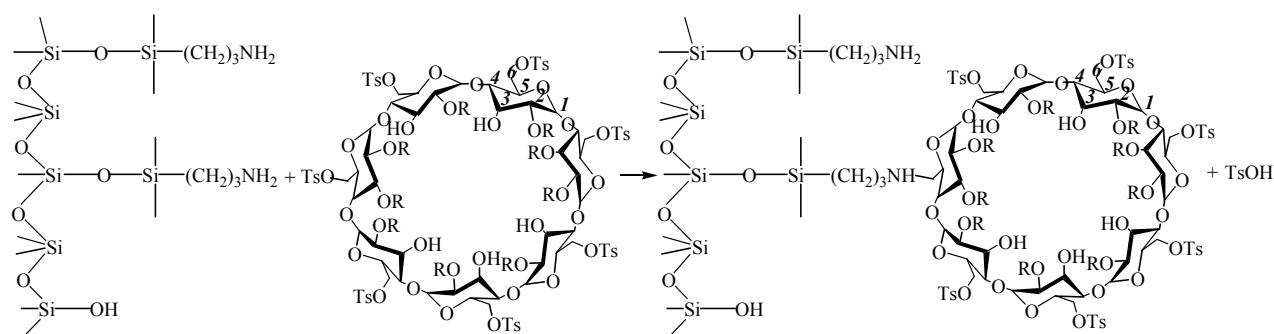


Fig. 2. IR spectra for adsorbent 3 before (b) and after (c) adsorption of mercury (II) ions. IR spectrum for bromine derivative of heptakis-(6-O-(toluenesulfonyl))- β -cyclodextrin (a).



vibrations of the C–H bonds in the hydrocarbon groups; at 1365 cm^{-1} , the band of the asymmetric valence vibrations of the S=O bond in the $R_1\text{--O--SO}_2\text{--}R_2$ groups [17–19].

In the IR spectrum of aminopropylsilica modified with bromine derivative of heptakis-(6-*O*-(toluenesulfonyl))- β -cyclodextrin (adsorbent 3) the absorption bands belonging to Br-Ts- β -CD, namely, the bands of the valence vibrations of the C=C bond (1491 cm^{-1}) and the C–Br bond (680 cm^{-1}), and also the absorption band at 1542 cm^{-1} of the secondary amino groups are registered (Fig. 2b).

The molecular area of Br-Ts- β -CD is equal to $7,24\text{ nm}^2$, the monolayer capacity is $0,026\text{ mmol/g}$. The grafting extent of bromine derivative of heptakis-(6-*O*-(toluenesulfonyl))- β -cyclodextrin makes up 38%:

The surface structure of investigated silica adsorbents is given in Scheme:

Structural and sorptional parameters and chemical composition of the surface layer of silica adsorbents are presented in Table 2.

The adsorption equilibrium for adsorbents 1 and 2 is achieved in 1 and 2,5 h, respectively. For adsorbent 3 equilibrium is already attained within 15 minutes. The uptake of mercury ions from $\text{Hg}(\text{NO}_3)_2$ solutions with a concentration $\sim 10^{-4}\text{ M}$ by hydroxylated silica (adsorbent 1) is negligible (Fig. 3), since at pH 1–3 practically all silanol groups are nonionized, and Hg (II) comes in two forms – Hg^{2+} and $\text{Hg}(\text{OH})^+$ [20]. As Hg (II) content in the solution increases by a factor of 10^1 only 25% of surface silanol groups of adsorbent 1 adsorb mercury (II) ions. Aminopropylsilica (adsorbent 2) forms complexes with mercury (II) cations [21] only at high concentrations of $\text{Hg}(\text{NO}_3)_2$ in equilibrium solutions, adsorption of mercury (II) from dilute solutions is not observed (Fig. 3). Modification of silica surface with Br-Ts- β -CD is accompanied by essential increase of adsorptive affinity to Hg (II). The amount of Hg (II) ions

taken up from dilute solutions is 4 times higher in comparison with the quantity of Br-Ts- β -CD fixed on the silica surface. Taking into account that adsorbents 1–3 have constant total amount of active centers (Table 2), but different chemical composition of their surface layer it may be supposed the formation of mixed-ligand complexes of mercury (II) [22] with participation of the

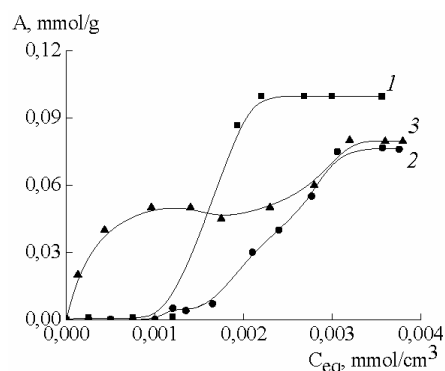


Fig. 3. Isotherms of mercury (II) ions adsorption on silica adsorbents 1–3: $\text{Hg}(\text{NO}_3)_2$ aqueous solutions from $2,5 \cdot 10^{-4}$ to $4,0 \cdot 10^{-3}\text{ M}$, adsorbent batch 0,1 g, solution volume 50 ml, 4 h, 22°C .

bromine-containing functional groups of the silica surface in the ratio of $[\text{Hg}] : [\text{Br}] : [\beta\text{-CD}] = 4 : 8 : 1$.

These results agree well with IR spectroscopy data. The IR spectrum of hydroxylated silica does not undergo any changes after adsorption of mercury (II) (Fig. 1b). In the IR spectrum of aminopropylsilica after adsorption of Hg (II) (Fig. 1d) only a little shift of the deformation vibrations band in the N–H bond for the primary amino groups (1571 cm^{-1}) into low-frequency range (1526 cm^{-1}) is observed. Evidently it is due to the complexing on the surface of adsorbent 2. The decrease of intensity of absorption bands of the valence vibrations of the C–H bonds and disappearance of absorption band of the C–Br

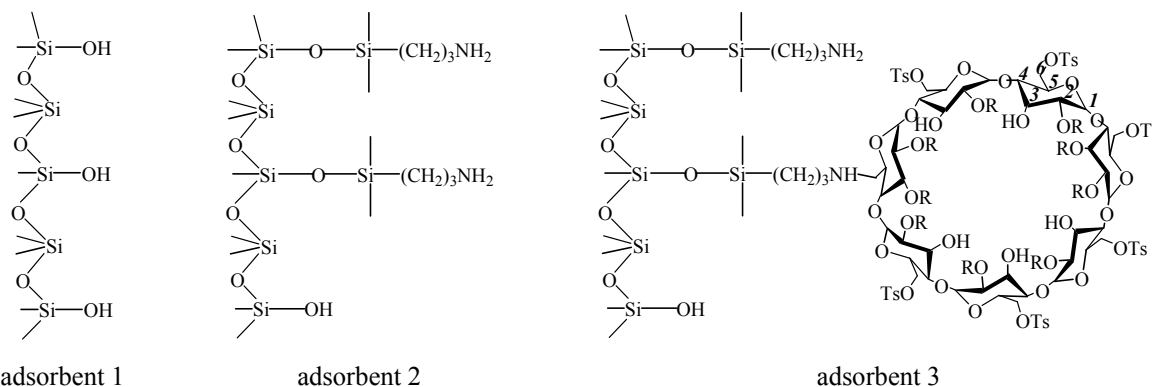


Table 1

Elemental analysis of modified β -cyclodextrins						
β -Cyclodextrin	Chemical composition	Molecular weight	Content of chemical elements, %			
			C	H	S	Br
Heptakis-(6- <i>O</i> -(toluenesulfonyl))- β -cyclodextrin	C ₉₁ H ₁₁₂ O ₄₉ S ₇	2214,30	49,51	5,23	10,05	–
Bromine derivative of heptakis-(6- <i>O</i> -(toluenesulfonyl))- β -cyclodextrin	C ₁₀₉ H ₁₂₁ O ₅₈ S ₇ Br ₉	3302,66	39,64	3,69	6,80	21,77

Table 2

Elemental analysis, chemical composition of surface layer, structural and sorptional parameters for silica adsorbents

Adsorbent	Specific surface area, m ² /g	Elemental analysis of surface layer, %					Content of functional groups, mmol/g			Ratio [Hg] : [functional group]
		C	N	H	Br	S	silanol	amino-propyl	β -cyclo-dextrin	
1	118						0,40	–	–	0,25
2	111	1,00	0,40	0,45	–	–	0,12	0,28	–	0,28
3	90	2,20	0,40	0,80	0,75	0,25	0,12	0,27	0,01	4,0

bond are observed in the IR spectrum of adsorbent 3 after adsorption of mercury (II) (Fig. 2c). Absorption band of the deformation vibrations of the N–H bond (1561 cm⁻¹) is shifted into low-frequency region (1529 cm⁻¹) as for aminopropylsilica. Hence, the main centers for adsorption of mercury (II) ions are chemically grafted molecules of Br-Ts- β -CD.

Conclusions

The way of chemical grafting of the bromine derivative of heptakis-(6-*O*-(toluenesulfonyl))- β -cyclodextrin on a surface of amorphous highly dispersed silica has been proposed. Structure and chemical composition of the surface of β -cyclodextrin-containing silica and intermediate products of its synthesis were established using IR spectroscopy and quantitative chemical analysis of surface compounds. The influence of silica surface layer structure on adsorption of Hg (II) from dilute aqueous solutions of Hg(NO₃)₂ (pH = 1–3) has been studied. It is shown that silanol and aminopropyl groups of silica adsorbents practically do not adsorb mercury (II) cations as they are nonionized and protonated, respectively. The main centers of Hg (II) adsorption are molecules of bromine derivative of heptakis-(6-*O*-(toluenesulfonyl))- β -cyclodextrin grafted onto silica surface. Adsorption of mercury (II) takes

place, apparently, through the formation of mixed-ligand complexes with participation of bromine-containing functional groups of the upper edge of β -cyclodextrin molecules. Supramolecular structures with the composition [Hg] : [Br] : [β -CD] = 4 : 8 : 1 are formed on a surface of β -cyclodextrin-containing silica.

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Кремнезем, модифікований бромпохідним гептакіс-(6-О-(толуолсульфоніл))- β -циклодекстрину: синтез, будова і адсорбційні властивості

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Здійснено багатостадійне хімічне модифікування поверхні кремнезему бромпохідним гептакіс-(6-О-(толуолсульфоніл))- β -циклодекстрину. За допомогою ІЧ спектроскопії та кількісного аналізу поверхневих сполук встановлено будову поверхні модифікованого кремнезему. Вивчено адсорбцію Hg (II) із розведених водних розчинів. Встановлено суттєве підвищення адсорбційної спорідненості кремнезему до іонів ртуті завдяки утворенню на його поверхні супрамолекулярних структур із хімічно іммобілізованим бромпохідним гептакіс-(6-О-(толуолсульфоніл))- β -циклодекстрину.

Ключові слова: поверхня кремнезему, β -циклодекстрин, іммобілізація, нітрат ртуті (II), адсорбція.