

UDC 544.723:[546.284-31:543.635.24]

L.A. Belyakova, D.Yu. Lyashenko, L.S. Dzyubenko, O.M. Shvets

## NANOPOROUS $\beta$ -CYCLODEXTRIN-CONTAINING SILICAS: SYNTHESIS, STRUCTURE AND PROPERTIES

Chuiko Institute of Surface Chemistry of National Academy of Sciences of Ukraine  
17 General Naumov Str., Kyiv, 03164, Ukraine, E-mail: mila.belyakova@gmail.com

Nanoporous  $\beta$ -cyclodextrin-containing silicas which differ in functional substituents of wide edge of attached cyclic oligosaccharide molecules (alcohol, bromoacetyl, thiosemicarbazidoacetyl groups) were synthesized. Chemical composition of surface layer of organosilicas and their sorptional parameters were determined using IR spectroscopy, isotherms of nitrogen ad-desorption, elemental, chemical and thermogravimetric analyses. Ranges of thermal and chemical stability of synthesized  $\beta$ -cyclodextrin-containing silicas were defined; a method of organosilicas regeneration was proposed. Activation energies of water removal from the inner cavities of  $\beta$ -cyclodextrins and from the surface of functional organosilicas were calculated. Distribution and selectivity coefficients for sorption of mercury(II), copper(II), lead(II), cadmium(II), and zinc(II) cations were computed.

**Keywords:** silica,  $\beta$ -cyclodextrin, chemical immobilization, sorption, heavy metal nitrates, IR spectroscopy, thermogravimetry, regeneration

### INTRODUCTION

Extraction of trace amounts of heavy metal ions and chemical analysis in the environmental objects is an important task because of their high toxicity [1]. Therefore, the synthesis of new sorption-active materials is still relevant. The most promising for these purposes are inorganic chelation materials. They combine in themselves high affinity of chemically grafted organic functional groups to ions being sorbed and good kinetic parameters of non-swelling matrices [2–4]. In addition, inorganic sorbents, as a rule, are more stable to external mechanical, chemical and thermal affects [3].

This paper presents the results of  $\beta$ -cyclodextrin-containing silicas synthesis and investigation of their surface and porous structures, thermal stability, and sorption affinity to mercury(II), copper(II), lead(II), cadmium(II), and zinc(II) cations from nitrate solutions.

### EXPERIMENTAL

**Materials.** Nanoporous amorphous silica – silochrome C-120 with specific surface area of  $133 \text{ m}^2 \cdot \text{g}^{-1}$ , average pore diameter of 48 nm and isolated silanol groups content of  $0.4 \text{ mmol} \cdot \text{g}^{-1}$  was a starting silica matrix for synthesis of organosilicas.  $\beta$ -Cyclodextrin ( $\beta$ -CD) “Fluka” with purity 99 % was used without additional

purification. Mercury(II), copper(II), lead(II), cadmium(II), and zinc(II) nitrates (“Merck”, purity 98 %) were used for sorption studies.

**Instruments.** Control of the chemical modification of the silica surface was undertaken using IR spectroscopy (Thermo Nicolet NEXUS FT-IR spectrophotometer), elemental (Elemental Analyzer EA 1110) and thermogravimetric (Thermoanalyzer Q-1500 D) analyses, as well as the potentiometric titration (Ionometer I-120.1) and chemical analysis of the surface intermediates and the final products of all reactions.

IR spectra of pressed plates (~30 mg) of starting and modified silicas were recorded over the spectral range  $4000\text{--}500 \text{ cm}^{-1}$ .

Total thermal analysis of functional organosilicas (batch weight 150–180 mg) was performed in the range  $20\text{--}1000 \text{ }^\circ\text{C}$  at a heating rate of  $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ . Registration of TG, DTG and TGA curves was realized simultaneously with sensitivity 500, 500, 100, respectively. Thermal analyses were carried out in air ensuring complete burning out of organic groups attached to silica surface. Quantity of grafted functional groups was determined from TG and DTG curves, and activation energies of dehydration  $E_{act}$  were calculated according to the equation:

$$E_{act} = (RT_o^2/b) \cdot 1/\tau,$$

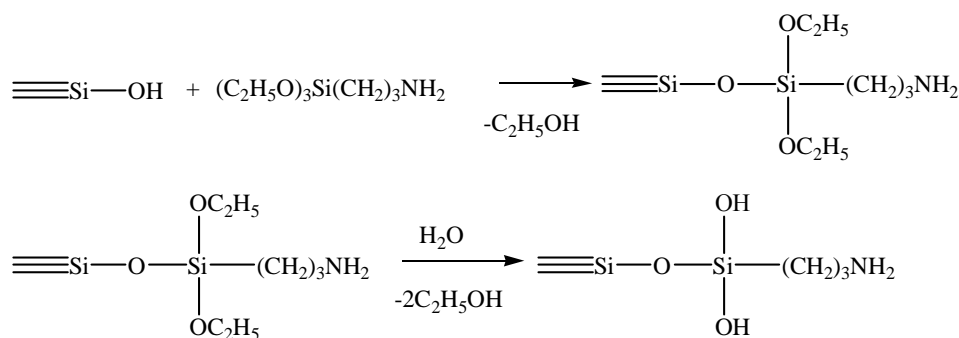
where  $R$  is universal gas constant,  $8.314 \text{ J}\cdot(\text{mol}\cdot\text{K})^{-1}$ ;  $T_o$  is a temperature of beginning of dehydration, K;  $b$  is a heating rate,  $\text{K}\cdot\text{min}^{-1}$ ;  $\tau$  is a time interval during which maximal dehydration rate is achieved, min [5].

Parameters of porous structure of starting and modified silicas were calculated from low-temperature nitrogen ad-desorption isotherms measured using a Sorptometer Kelvin 1042. Organosilicas were preliminarily evacuated at  $190^\circ\text{C}$  during 20 h.

Sorption of cations was studied by the method of individual batches from  $10^{-4}$ – $10^{-3}$  M nitrate solutions with  $\text{pH}\sim 1$  at  $22^\circ\text{C}$  under static conditions [6].

Distribution coefficients of cations between solid and liquid phases  $K_d$  [7] were determined as:

$$K_d = a_{eq} / C_{eq},$$



**Scheme 1.** Preparation of aminopropylsilica

For this purpose silochrome preliminarily was dried at  $400^\circ\text{C}$  for 8 h, placed into a three-necked reactor with a stirrer and a reflux condenser, and suspended in a small amount of toluene at room temperature for 40 min. After that,  $\gamma$ -aminopropyltriethoxysilane (three-fold excess with respect to the content of silanol groups on a silica surface) was added. The reaction mixture was stirred at  $110^\circ\text{C}$  for 6 h. Synthesized aminopropylsilica was filtered and washed with toluene until the absence of silane (absence of a violet color on addition of ninhydrin), then acetone, distilled water (for hydrolysis of ether groups), and again acetone. The resulting aminopropylsilica was dried in air at  $100^\circ\text{C}$  for 2 h and kept in a desiccator before use.

Interaction of aminopropylsilica with mono-(6-*O*-(toluenesulfonyl))- $\beta$ -CD (Scheme 2,  $\beta$ -CD-1-silica, Table 1) or bromoacetyl derivative of heptakis-(6-*O*-(toluenesulfonyl))- $\beta$ -CD (Scheme 2,

where  $a_{eq}$  is the equilibrium adsorption,  $\text{mmol}\cdot\text{g}^{-1}$ ;  $C_{eq}$  is the equilibrium concentration of adsorptive,  $\text{mmol}\cdot\text{ml}^{-1}$ .

Selectivity coefficients  $\beta$  [7] were calculated by formula:

$$\beta = K_{d \text{ Me}} / K_{d \text{ (Ca + Mg)}},$$

where  $K_{d \text{ Me}}$  is the distribution coefficient for metal cations;  $K_{d \text{ (Ca + Mg)}}$  is the distribution coefficient for hardness salts at their sorption from binary solutions [8].

## RESULTS AND DISCUSSION

**Synthesis of  $\beta$ -cyclodextrin-containing silicas** was performed using consecutive reactions in the surface layer of silochrome C-120. The first step (Scheme 1) was the interaction of starting silica with  $\gamma$ -aminopropyltriethoxysilane:

$\beta$ -CD-2-silica) was realized under conditions of optimal running of the reaction of electrophilic substitution of proton in aminopropyl groups with  $\beta$ -cyclodextrin ones ( $60^\circ\text{C}$ , 96 h, triethylamine as a catalyst, pyridine as a solvent) [9–11] (Scheme 2).

The obtained products were filtered, washed with toluene, acetone, and dried in air at  $100^\circ\text{C}$  for 2 h (Table 2).

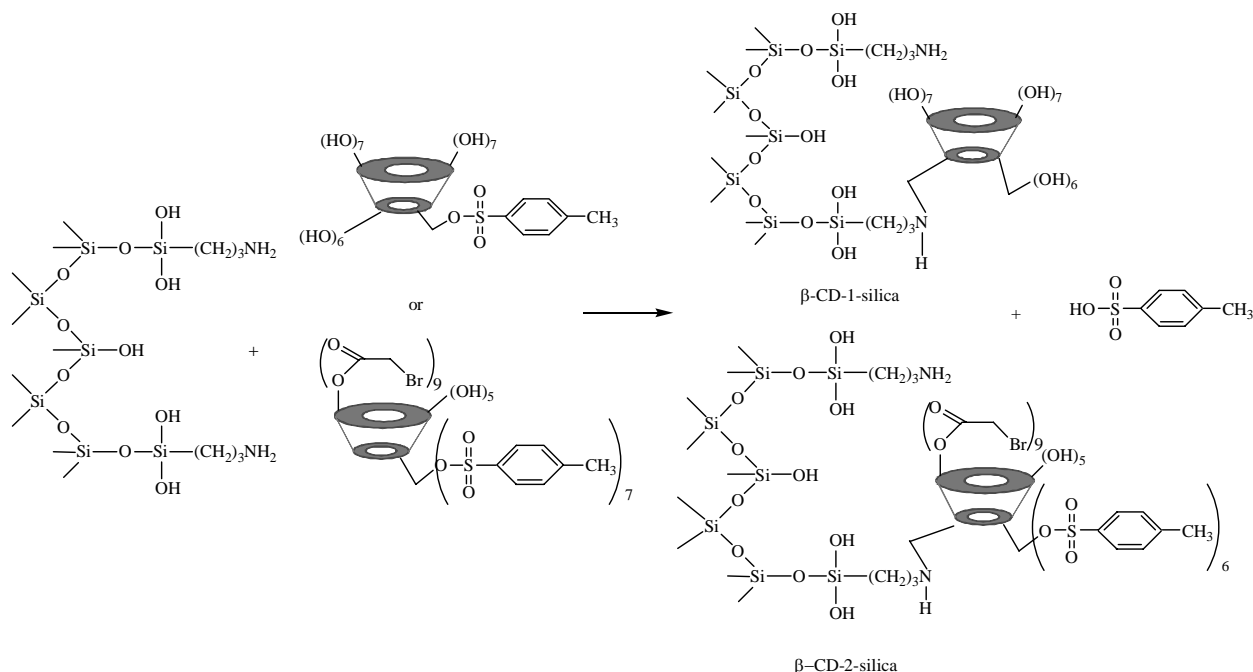
$\beta$ -CD-3-silica with thiosemicarbazidoacetyl groups (Scheme 3) was obtained from  $\beta$ -CD-2-silica ( $110^\circ\text{C}$  6 h, dry toluene is a solvent for thiosemicarbazide). The resulting product was washed with toluene, acetone, and dried in air.

Chemical reactions on silica surface were proved by IR spectroscopy, and also by elemental and chemical analyses of reaction products.

**IR spectroscopy.** IR spectra of starting silica and after its modification with aminopropyl (Scheme 1) and  $\beta$ -cyclodextrin (Schemes 2, 3) groups are shown in Fig. 1.

Characteristic absorption bands at 3375, 3310 and 1590  $\text{cm}^{-1}$  belonging to the stretching and deformation vibrations of the N–H bonds in the grafted amino groups and absorption bands at

2930, 2880 and 1455, 1395  $\text{cm}^{-1}$  corresponding to the valence and deformation vibrations of the C–H bonds in the hydrocarbon groups are registered for aminopropylsilica (Fig. 1, curve 2) [12, 13].



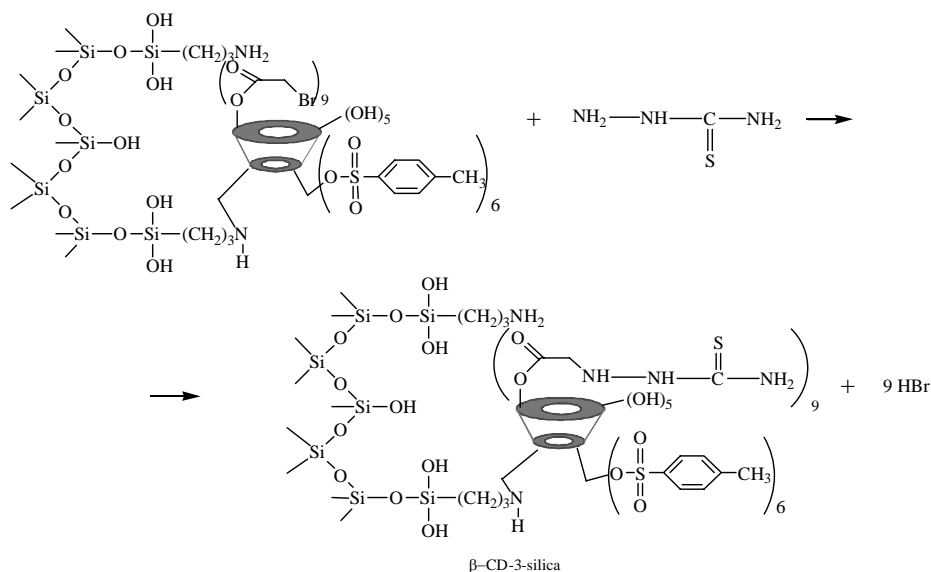
**Scheme 2.** Synthesis of functional  $\beta$ -cyclodextrin-containing silicas

**Table 1.**  $\beta$ -Cyclodextrin and its functional derivatives

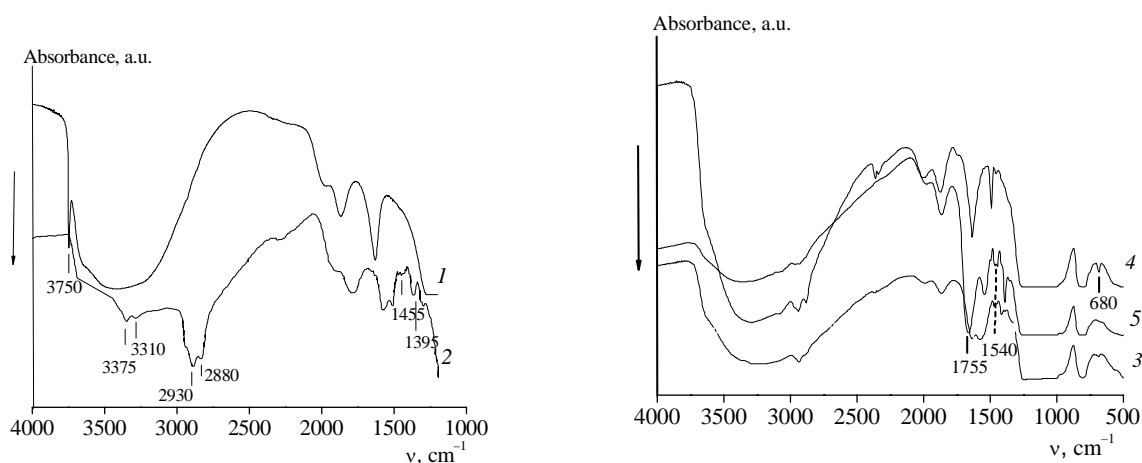
| $\beta$ -Cyclodextrins                 | Chemical formula   | Molecular mass | Chemical elements content, % |       |       |       |
|--|--|----------------|------------------------------|-------|-------|-------|
|  |  |                | H                            | C     | Br    | S     |
| $\beta$ -CD                            | $\text{C}_{42}\text{H}_{70}\text{O}_{35}$                        | 1135.18        | 6.22                         | 44.44 | –     | –     |
| mono-tosyl- $\beta$ -CD                | $\text{C}_{49}\text{H}_{76}\text{O}_{37}\text{S}$                | 1289.17        | 7.06                         | 50.47 | –     | 1.45  |
| heptakis-(6-O-p-tosyl)- $\beta$ -CD    | $\text{C}_{91}\text{H}_{112}\text{O}_{49}\text{S}_7$             | 2214.25        | 23                           | 49.51 | –     | 10.05 |
| Br-heptakis-(6-O-p-tosyl)- $\beta$ -CD | $\text{C}_{109}\text{H}_{121}\text{O}_{58}\text{S}_7\text{Br}_9$ | 3302.66        | 3.69                         | 39.64 | 21.77 | 6.80  |

**Table 2.** Structural and sorptional parameters of synthesized organosilicas

| Organosilica         | $S_{\text{BET}}, \text{m}^2 \cdot \text{g}^{-1}$ | $V_{\text{pores}}, \text{cm}^3 \cdot \text{g}^{-1}$ |                  | $d_{\text{av}}, \text{nm}$ | Content of functional groups, $\text{mmol} \cdot \text{g}^{-1}$ |             |                       |
|----------------------|--|---|------------------|----------------------------|---|-------------|-----------------------|
|                      |  | $V_{\Sigma}$  | $V_{\text{BJH}}$ |                            | silanol   | aminopropyl | $\beta$ -cyclodextrin |
| Initial silica       | 133  | 0.80  | 0.80             | 48                         | 0.40  | –           | –                     |
| Aminopropylsilica    | 114  | 0.75  | 0.72             | 33                         | 0.20  | 0.20        | –                     |
| $\beta$ -CD-1-silica | 98   | 0.58  | 0.87             | 29                         | 0.20  | 0.18        | 0.02                  |
| $\beta$ -CD-2-silica | 95   | 0.50  | 0.94             | 24                         | 0.20  | 0.19        | 0.01                  |
| $\beta$ -CD-3-silica | 90   | 0.42  | 0.93             | 17                         | 0.20  | 0.19        | 0.01                  |



**Scheme 3.** Functionalization of  $\beta$ -cyclodextrin-containing silica with thiosemicarbazide



**Fig. 1.** IR spectra of starting silica (1), aminopropylsilica (2),  $\beta$ -CD-1-silica (3),  $\beta$ -CD-2-silica (4), and  $\beta$ -CD-3-silica (5)

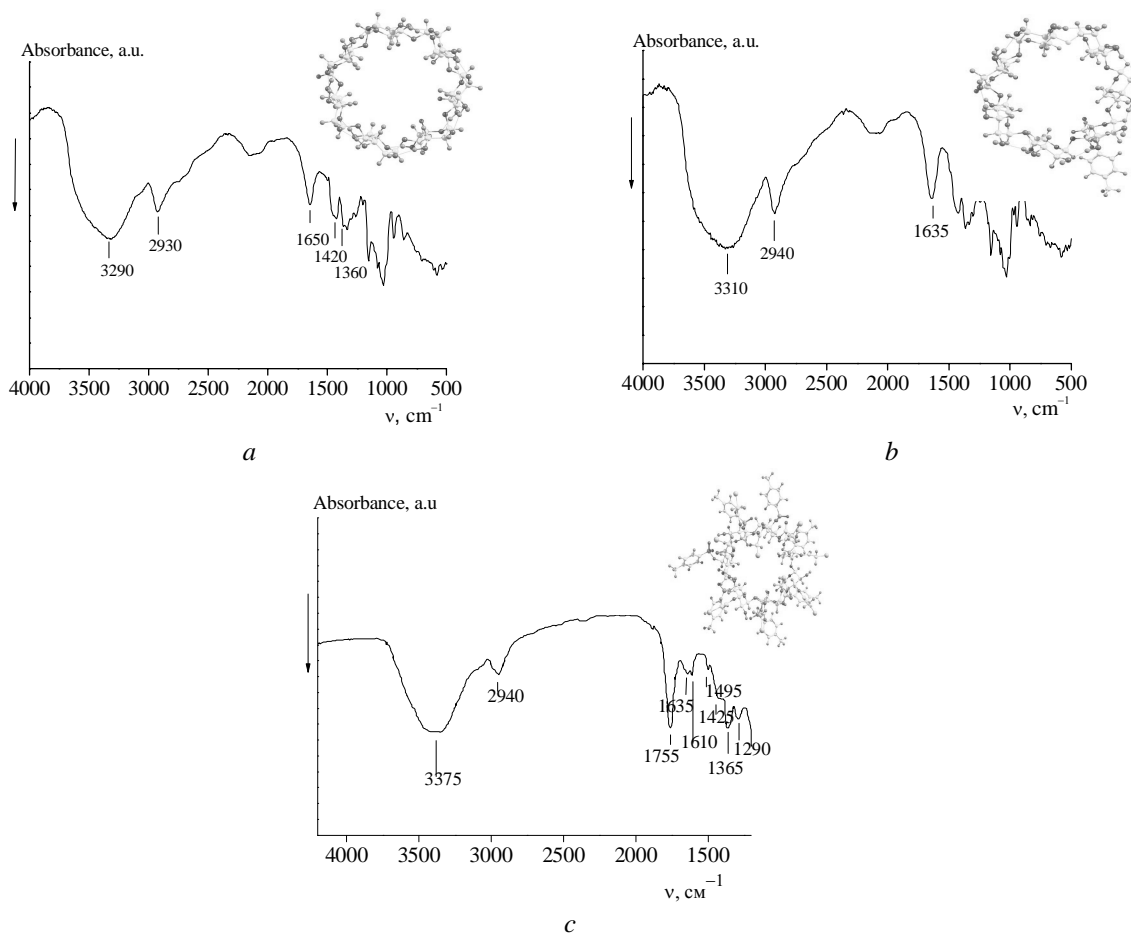
In the IR spectra of mono-(6-*O*-(toluenesulfonyl))- $\beta$ -CD and heptakis-(6-*O*-(toluenesulfonyl))- $\beta$ -CD (Fig. 2) there are following absorption bands: at  $3375\text{ cm}^{-1}$ , the band of the stretching vibrations of the O–H bond in the secondary hydroxyl groups of  $\beta$ -CDs connected by hydrogen bonds [14, 15]; at  $2940\text{ cm}^{-1}$ , the band of the valence vibrations of the C–H bond in the methylene groups; at  $1635\text{ cm}^{-1}$ , the band of the deformation vibrations of the O–H bonds in the COH groups and/or of the water molecules; at  $1610$  and  $1495\text{ cm}^{-1}$ , the bands of the valence vibrations of the C=C bond in the benzene ring of the toluenesulfonyl groups; at  $1425$  and  $1290\text{ cm}^{-1}$ , the bands of the deformation vibrations of the C–H bonds in the hydrocarbon groups; at  $1365\text{ cm}^{-1}$ , the band of the

asymmetric valence vibrations of the S=O bond in the *p*-toluenesulfonyl groups [14, 16, 17]. Besides, the IR spectrum of bromoacetyl derivative of heptakis-(6-*O*-(toluenesulfonyl))- $\beta$ -CD (Fig. 2, c) shows absorption bands of the valence vibrations of the C=O ( $1755\text{ cm}^{-1}$ ) and C–Br ( $680\text{ cm}^{-1}$ ) bonds in the bromoacetyl groups.

The IR spectrum of aminopropylsilica after interaction with mono-(6-*O*-(toluenesulfonyl))- $\beta$ -CD (Fig. 1, curve 3) has no absorption bands belonging to the toluenesulfonyl group, and the absorption band at  $1540\text{ cm}^{-1}$  appears to correspond to the deformation vibrations of the N–H bond in the secondary amino groups. Hence, the grafting of mono-(6-*O*-(toluenesulfonyl))- $\beta$ -CD takes place on the narrow edge of  $\beta$ -CD (Scheme 2). Bromoacetyl

derivative of heptakis-(6-*O*-(toluenesulfonyl))- $\beta$ -CD reacts with aminopropylsilica in the same manner (Scheme 2). In the IR spectrum of  $\beta$ -CD-2-silica there are also the absorption bands at 1490 and

680  $\text{cm}^{-1}$  belonging to the valence vibrations of the C=C and C-Br bonds in functional groups of grafted  $\beta$ -cyclodextrin molecules (Fig. 1, curve 4).



**Fig. 2.** IR spectra of  $\beta$ -cyclodextrin (a), mono-(6-*O*-(toluenesulfonyl))- $\beta$ -CD (b), and bromoacetyl derivative of heptakis-(6-*O*-(toluenesulfonyl))- $\beta$ -CD (c)

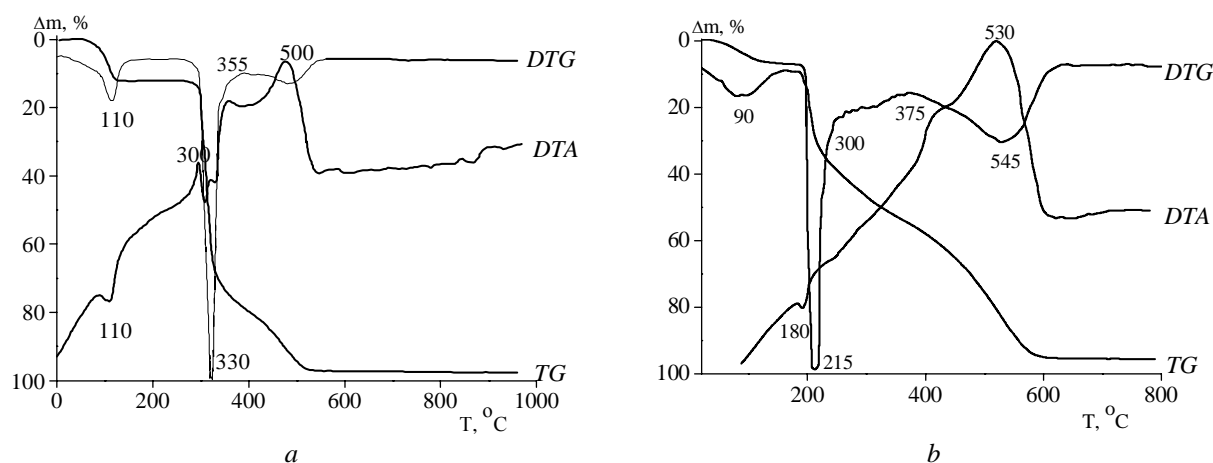
After interaction of  $\beta$ -CD-2-silica with thiosemicarbazide in the IR spectrum of modified silica ( $\beta$ -CD-3-silica) there is no absorption band of the valence vibrations of the C-Br ( $680 \text{ cm}^{-1}$ ) bond of bromoacetyl groups (Fig. 1, curve 5). Moreover, the intensity of the absorption band at  $1540 \text{ cm}^{-1}$  (secondary amino groups) significantly increases (Fig. 1, curve 5). These changes in the IR spectrum indicate on the chemical reaction of nucleophilic substitution between side bromoacetyl groups of wide edge of grafted  $\beta$ -CD molecules and thiosemicarbazide (Scheme 3).

**Thermogravimetric analysis of  $\beta$ -cyclodextrins and  $\beta$ -cyclodextrin-containing silicas.** On DTA curve of the  $\beta$ -CD thermogram (Fig. 3, a) four thermoeffects are observed: one

endothermic effect with maximum at  $110 \text{ }^\circ\text{C}$  and three exothermic effects ( $300\text{--}330$ ,  $355$ ,  $500 \text{ }^\circ\text{C}$ ) accompanied by weight loss on TG and DTG curves. Weight loss up to  $200 \text{ }^\circ\text{C}$  equals 11 %, in the range of  $200\text{--}450 \text{ }^\circ\text{C}$  it is 74 % and higher than  $450 \text{ }^\circ\text{C}$  – 15 % (Table 3). Endothermic effect corresponds to water removal from the inner cavities of  $\beta$ -cyclodextrin molecules. Its content, according to literature data [14], is 8–11 molecules. The experimental results (weight loss of 11 %) agree well with calculated data (11.26 %): there are 8 water molecules in the cavity of  $\beta$ -CD. The exothermic effect with two maxima ( $300$ ,  $330 \text{ }^\circ\text{C}$ ) is logically attributed to oxidative destruction of side primary and secondary alcohol groups (Fig. 3, a). However, weight loss in the range of

200–450 °C is 74 % that significantly exceeds the content of primary and secondary alcohol groups of  $\beta$ -CD molecule (Tables 3, 4). Consequently, it can be argued that desorption of glucopiranos rings begins already in this temperature interval (exoeffect with maximum at 355 °C) and ends at 600 °C (exoeffect with maximum at 500 °C).

Removal of water molecules from the inner cavity of bromoacetyl derivative of heptakis-(6-*O*-(toluenesulfonyl))- $\beta$ -CD and decomposition of residual secondary alcohol groups occur, mainly, before 200 °C. Oxidative destruction of *p*-toluenesulfonyl and bromoacetyl groups takes place, mostly, at 200–450 °C. Glucopiranos rings break up higher than 450 °C (Fig. 3, *b*).



**Fig. 3.** Thermal curves of  $\beta$ -cyclodextrin (*a*) and bromoacetyl derivative of heptakis-(6-*O*-toluenesulfonyl)- $\beta$ -CD (*b*)

**Table 3.** Temperature ranges of destruction of  $\beta$ -cyclodextrins and organosilicas

| Compound                 | Weight loss at heating, % |            |            |
|--------------------------|---------------------------|------------|------------|
|                          | 25–200 °C                 | 200–450 °C | 450–800 °C |
| $\beta$ -CD              | 11                        | 74         | 15         |
| bromoacetyl- $\beta$ -CD | 6                         | 58         | 36         |
| $\beta$ -CD-1-silica     | 25                        | 57         | 18         |
| $\beta$ -CD-2-silica     | 30                        | 56         | 14         |
| $\beta$ -CD-3-silica     | 21                        | 64         | 15         |

**Table 4.** Composition of  $\beta$ -cyclodextrins

| $\beta$ -Cyclodextrin  | Content of water and functional substituents in $\beta$ -CD, % |                     |       |  |                       |                   |
|--|--|---------------------|-------|--|-----------------------|-------------------|
|  | H <sub>2</sub> O   | -CH <sub>2</sub> OH | -CHOH | -SO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> | -COCH <sub>2</sub> Br | glucopiranos ring |
| $\beta$ -CD<br>C <sub>42</sub> H <sub>70</sub> O <sub>35</sub>   | 11.26  | 16.86               | 32.83 | –  | –                     | 39.04             |
| bromoacetyl- $\beta$ -CD<br>C <sub>109</sub> H <sub>121</sub> O <sub>58</sub> S <sub>7</sub> Br <sub>9</sub> | 4.36   | –                   | 4.54  | 32.85  | 33.24                 | 25.01             |

Interpretation of obtained results is consistent with the data of Tables 3 and 4. Calculated values of thermal degradation fragments coincide with the data of thermogravimetric analysis. The main decomposition of  $\beta$ -cyclodextrins occurs at 200–450 °C.

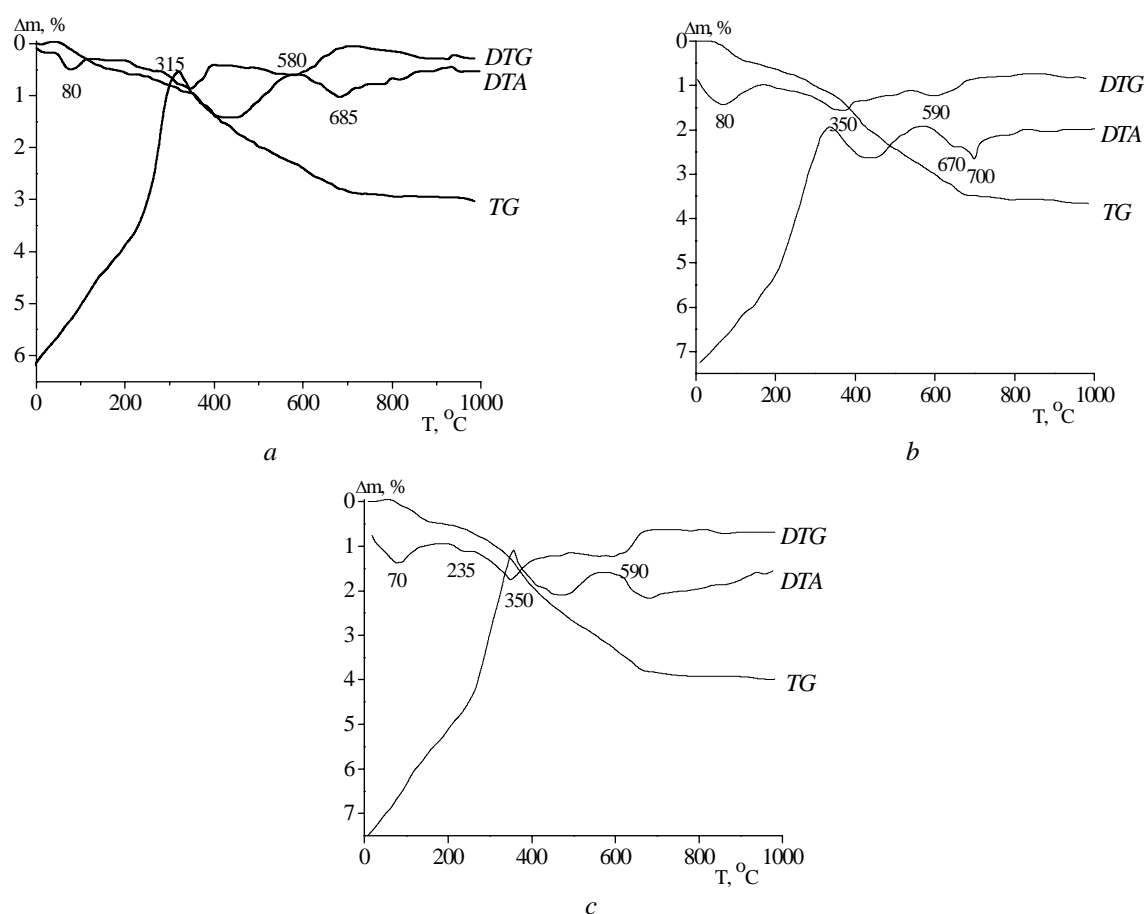
The type of functional  $\beta$ -cyclodextrins destruction, in general, is retained also after their chemical immobilization on 3-aminopropylsilica

surface. At the same time, there are some peculiarities. Firstly, weight loss for  $\beta$ -cyclodextrin-containing silicas (from 25 to 200 °C) is significantly higher than quantity of water in the inner cavities of immobilized  $\beta$ -cyclodextrin molecules. It can be associated with condensation of the secondary silanol groups which are formed as a result of hydrolysis of side ether groups of

grafted 3-aminopropyl radicals [3]. For  $\beta$ -CD-1-silica (Fig. 4, *a*) in interval from 200 to 450 °C decomposition of the primary and secondary alcohol groups of  $\beta$ -cyclodextrin takes place, and disruption of glucopiranosose rings begins. At 450–800 °C decomposition of chemically immobilized aminopropyl groups is also observed [3].

For  $\beta$ -CD-2-silica (Fig. 4, *b*) removal of water from the cavities of grafted molecules of bromoacetyl derivative of heptakis-(6-*O*-(toluenesulfonyl))- $\beta$ -CD, condensation of the secondary silanol groups, partial decomposition of

toluenesulfonyl and alcohol groups of  $\beta$ -cyclodextrin occur up to 200 °C. At 200–450 °C destruction of functional groups of wide side of grafted molecules of functionalized  $\beta$ -cyclodextrin (secondary alcohol and bromoacetyl groups) ends, and decomposition of glucopiranosose rings begins. Within 450–800 °C destruction of glucopiranosose rings finishes, and also destruction of aminopropyl radicals ( $T_{\max} = 590$  °C) takes place. Superposition of these two processes appears as exothermic effect with maximum at 590 °C and smooth weight loss up to 800 °C.



**Fig. 4.** Thermal curves of  $\beta$ -CD-1-silica (*a*),  $\beta$ -CD-2-silica (*b*), and  $\beta$ -CD-3-silica (*c*)

Thermodestruction of  $\beta$ -CD-3-silica (Fig. 4, *c*) occurs in the same way as for  $\beta$ -CD-2-silica. Thiosemicarbazidoacetyl groups decompose at 200–450 °C.

Calculated values of activation energy of water removal from  $\beta$ -cyclodextrins and  $\beta$ -cyclodextrin-containing silicas are higher than that for 3-aminopropylsilica which was used as initial carrier for synthesis of  $\beta$ -CD-materials. Activation

energies for  $\beta$ -cyclodextrin-containing silicas have intermediate values (Table 5). This may be due to removal of adsorbed water as well as water from the inner cavities of grafted molecules of  $\beta$ -cyclodextrins on the  $\beta$ -CD-silicas surface.

Thus, synthesized  $\beta$ -cyclodextrin-containing silicas have high thermal stability. The nature of their stepwise destruction depends on the chemical composition of grafted  $\beta$ -cyclodextrins.

**Table 5.** Activation energy of water removal from  $\beta$ -cyclodextrins and organosilicas

| Compound                 | $T_{05}$ , K | $T_{max}$ , K | $1/\tau$ , min <sup>-1</sup> | $E_{act}$ , kJ/mol |
|--------------------------|--------------|---------------|------------------------------|--------------------|
| $\beta$ -CD              | 333          | 383           | 0.200                        | 18.4               |
| bromoacetyl- $\beta$ -CD | 332          | 363           | 0.200                        | 18.3               |
| aminopropylsilica        | 298          | 343           | 0.133                        | 9.2                |
| $\beta$ -CD-1-silica     | 320          | 353           | 0.154                        | 13.1               |
| $\beta$ -CD-2-silica     | 320          | 353           | 0.152                        | 12.9               |
| $\beta$ -CD-3-silica     | 311          | 343           | 0.179                        | 14.4               |

**Sorption of metal cations by  $\beta$ -cyclodextrin-containing silicas.** Obtained  $\beta$ -cyclodextrin-containing silicas were tested in a series of sorption of cations, including those of heavy metals, from the weakly acidic nitrate solutions. The sorbents had good chemical stability: contact with 5 M nitric acid for 24 h did not reduce static capacities of  $\beta$ -CD-silicas. Sorption equilibrium is reached within 5–30 min of contact with solutions of nitrate

salts. Sorbents can withstand at least five cycles of sorption-desorption without loss of capacity. Nitrate-anions sorption occurs simultaneously with absorption of cations. As a result, supermolecules are formed on the silica surface. Their chemical composition depends on the affinity of  $\beta$ -cyclodextrin-containing silicas to certain cations (Table 6).

**Table 6.** Characteristics of zinc(II), cadmium(II), lead(II), copper(II), and mercury(II) sorption from aqueous nitrate solutions

| Sorbent                     | Distribution coefficient $K_d$ , ml·g <sup>-1</sup> | Chemical composition of supramolecular structures  | Selectivity coefficient, $\beta_{Me/(Ca+Mg)**}$ |
|-----------------------------|---|--|---|
| Zn(II) ( $\eta^* = 10.88$ ) |   |  |   |
| $\beta$ -CD-1-silica        | 1250  | C <sub>42</sub> H <sub>69</sub> O <sub>34</sub> · 7 Zn(NO <sub>3</sub> ) <sub>2</sub>                                    | 310   |
| $\beta$ -CD-2-silica        | 860   | C <sub>102</sub> H <sub>114</sub> O <sub>55</sub> S <sub>6</sub> Br <sub>9</sub> · 12 Zn(NO <sub>3</sub> ) <sub>2</sub>  | 2000  |
| $\beta$ -CD-3-silica        | 565   | C <sub>111</sub> H <sub>150</sub> O <sub>55</sub> S <sub>15</sub> N <sub>27</sub> · 5 Zn(NO <sub>3</sub> ) <sub>2</sub>  | 3770  |
| Cd(II) ( $\eta = 10.29$ )   |   |  |   |
| $\beta$ -CD-1-silica        | 125   | C <sub>42</sub> H <sub>70</sub> O <sub>34</sub> · Cd(NO <sub>3</sub> ) <sub>2</sub>                                      | 30  |
| $\beta$ -CD-2-silica        | 200   | C <sub>98</sub> H <sub>112</sub> O <sub>53</sub> S <sub>6</sub> Br <sub>9</sub> · 4 Cd(NO <sub>3</sub> ) <sub>2</sub>    | 460   |
| $\beta$ -CD-3-silica        | 340   | C <sub>107</sub> H <sub>148</sub> O <sub>53</sub> S <sub>15</sub> N <sub>27</sub> · 5 Cd(NO <sub>3</sub> ) <sub>2</sub>  | 2270  |
| Pb(II) ( $\eta = 8.46$ )    |   |  |   |
| $\beta$ -CD-1-silica        | 200   | C <sub>42</sub> H <sub>70</sub> O <sub>34</sub> · 2 Pb(NO <sub>3</sub> ) <sub>2</sub>                                    | 50  |
| $\beta$ -CD-2-silica        | 320   | C <sub>98</sub> H <sub>112</sub> O <sub>53</sub> S <sub>6</sub> Br <sub>9</sub> · 6 Pb(NO <sub>3</sub> ) <sub>2</sub>    | 775   |
| $\beta$ -CD-3-silica        | 400   | C <sub>107</sub> H <sub>148</sub> O <sub>53</sub> S <sub>15</sub> N <sub>27</sub> · 8 Pb(NO <sub>3</sub> ) <sub>2</sub>  | 2670  |
| Cu(II) ( $\eta = 8.27$ )    |   |  |   |
| $\beta$ -CD-1-silica        | 250   | C <sub>42</sub> H <sub>70</sub> O <sub>34</sub> · 3 Cu(NO <sub>3</sub> ) <sub>2</sub>                                    | 60  |
| $\beta$ -CD-2-silica        | 320   | C <sub>98</sub> H <sub>112</sub> O <sub>53</sub> S <sub>6</sub> Br <sub>9</sub> · 7 Cu(NO <sub>3</sub> ) <sub>2</sub>    | 775   |
| $\beta$ -CD-3-silica        | 1900  | C <sub>107</sub> H <sub>148</sub> O <sub>53</sub> S <sub>15</sub> N <sub>27</sub> · 12 Cu(NO <sub>3</sub> ) <sub>2</sub> | 12670   |
| Hg(II) ( $\eta = 7.70$ )    |   |  |   |
| $\beta$ -CD-1-silica        | 320   | C <sub>42</sub> H <sub>70</sub> O <sub>34</sub> · 4 Hg(NO <sub>3</sub> ) <sub>2</sub>                                    | 80  |
| $\beta$ -CD-2-silica        | 450   | C <sub>98</sub> H <sub>112</sub> O <sub>53</sub> S <sub>6</sub> Br <sub>9</sub> · 8 Hg(NO <sub>3</sub> ) <sub>2</sub>    | 1050  |
| $\beta$ -CD-3-silica        | 2940  | C <sub>107</sub> H <sub>148</sub> O <sub>53</sub> S <sub>15</sub> N <sub>27</sub> · 14 Hg(NO <sub>3</sub> ) <sub>2</sub> | 19600   |

\* absolute hardness [18]

\*\* concentration of hardness salts is 10<sup>-1</sup> M

Sorption affinity rows of  $\beta$ -cyclodextrin-containing silicas for cations of mercury(II), copper(II), lead(II), cadmium(II), and zinc(II) do not contradict the theory of hard and soft acids and bases [18–20] (Table 6):

$\beta$ -CD-1-silica Cd(II) < Pb(II) < Cu(II) < Hg(II) << Zn(II);

$\beta$ -CD-2-silica Cd(II) < Pb(II), Cu(II) < Hg(II) < Zn(II);

$\beta$ -CD-3-silica Cd(II) < Pb(II) < Zn(II) << Cu(II) << Hg(II).

This confirms the realization of surface complex formation with  $\beta$ -CD-silicas participation. In the presence of hardness salts the affinity of  $\beta$ -CD-silicas to heavy metal cations increases because grafted  $\beta$ -cyclodextrins contain several active adsorption centers in their structures



(Table 6). Furthermore, cations of heavy metals may be separated by  $\beta$ -CD-3-silica. Thus, selectivity coefficients  $\beta_{Hg/Cd}$ ,  $\beta_{Hg/Pb}$  and  $\beta_{Hg/Zn}$  are 8.6, 7.4, and 5.2, respectively.

### CONCLUSIONS

Chemical composition and structure of the surface of functional  $\beta$ -cyclodextrin-containing silicas were determined. Intervals of thermal and

chemical stability of silica materials were found. Parameters of mercury(II), copper(II), lead(II), cadmium(II), and zinc(II) sorption from nitrate solutions were calculated. The rows of sorption affinity towards various cations for synthesized  $\beta$ -cyclodextrin-containing silicas were defined. Regeneration conditions which allow the use of synthesized  $\beta$ -cyclodextrin-silicas repeatedly were found.

## Нанопористі $\beta$ -циклодекстринвмісні кремнеземи: синтез, будова та властивості

Л.О. Белякова, Д.Ю. Ляшенко, Л.С. Дзюбенко, О.М. Швець

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

*Синтезовано нанопористі  $\beta$ -циклодекстринвмісні кремнеземи, які різняться функціональними замісниками широкого краю прищеплених молекул циклічних олігосахаридів (спиртові, бромоацетильні, тиосемікарбазидоацетильні групи). Хімічний склад поверхневого шару органокремнеземів та їх сорбційні параметри визначено з використанням ІЧ-спектроскопії, ізотерм ад-десорбції азоту, елементного, хімічного і термогравіметричного аналізу. Встановлено діапазони термічної та хімічної стійкості синтезованих  $\beta$ -циклодекстринвмісних кремнеземів; запропоновано метод регенерації органокремнеземів. Розраховано енергії активації видалення води з внутрішніх порожнин  $\beta$ -циклодекстринів і з поверхні функціональних органокремнеземів. Визначено коефіцієнти розподілу і селективності сорбції катіонів ртуті(II), міді(II), свинцю(II), кадмію(II) та цинку(II).*

**Ключові слова:** *кремнезем,  $\beta$ -циклодекстрин, хімічна іммобілізація, сорбція, нітрати важких металів, ІЧ спектроскопія, термогравіметрія, регенерація*

## Нанопористые $\beta$ -циклодекстринсодержащие кремнеземы: синтез, строение и свойства

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

*Інститут хімії поверхності ім. А.А. Чуйко Національної академії наук України  
ул. Генерала Наумова, 17, Киев, 03164, Украина, mila.belyakova@gmail.com*

*Синтезированы нанопористые  $\beta$ -циклодекстринсодержащие кремнеземы, отличающиеся функциональными заместителями широкого края привитых молекул циклических олигосахаридов (спиртовые, бромоацетильные, тиосемікарбазидоацетильные группы). Химический состав поверхностного слоя органокремнеземов и их сорбционные параметры определены с использованием ИК-спектроскопии, изотерм ад-десорбции азота, элементного, химического и термогравиметрического анализа. Установлены диапазоны термической и химической устойчивости синтезированных  $\beta$ -циклодекстринсодержащих кремнеземов; предложен метод регенерации органокремнеземов. Рассчитаны энергии активации удаления воды из внутренних полостей  $\beta$ -циклодекстринов и с поверхности функциональных органокремнеземов. Вычислены коэффициенты распределения и селективности сорбции катионов ртуті(II), меди(II), свинца(II), кадмия(II) и цинка(II).*

**Ключевые слова:** *кремнезем,  $\beta$ -циклодекстрин, химическая иммобилизация, сорбция, нитраты тяжелых металлов, ИК спектроскопия, термогравиметрия, регенерация*

REFERENCES

1. State sanitary rules and norms intended for human consumption, Ofits. Visn. Ukraine, 2010, N 51 (in Ukrainian).
2. *Iler R.K.* The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemistry of Silica, Wiley-Interscience, New York, 1979, 866 p.
3. *Tertykh V.A., Belyakova L.A.* Chemical Reactions Involving Silica Surface, Naukova Dumka, Kiev, 1991, 264 p. (in Russian).
4. *Vansant E.F., Van der Voort P., Vrancken K.C.* Characterization and Chemical Modification on the Silica Surface, Elsevier, Amsterdam, 1995, 556 p.
5. *Piloyan G.O., Ryabchikov J.D., Novikova O.S.* Determination of activation energies of chemical reactions by differential thermal analysis, Nature, 212 (1966) 1229.
6. *Helfferich F.G.* Ion Exchange, McGraw-Hill, New York, 1962, 624 p.
7. *Marhol M.* Ion Exchangers in Analytical Chemistry. Their Properties and Use in Inorganic Chemistry, Academia, Prague, 1982, 520 p.
8. *Belyakova L.A., Lyashenko D.Yu., Shvets A.N.* Sorption of Cd(II) from multicomponent nitrate solutions by functional organosilicas, J. Water Chem. Techn., 36 (2014) 56.
9. *Belyakova L.A., Kazdobin K.A., Belyakov V.N. et al.* Synthesis and properties of supramolecular systems based on silica, J. Colloid Interface Sci., 283 (2005) 488.
10. *Belyakova L.A., Lyashenko D.Yu., Varvarin A.M. et al.* Features of the interaction of silica with tosyl- $\beta$ -cyclodextrin, Ukr. Chem. J., 71 (2005) 86 (in Russian).
11. *Belyakova L.A., Lyashenko D.Yu.* Zinc(II) sorption on nanoporous  $\beta$ -cyclodextrin-containing organosilicas, Chemistry, Physics and Technology of Surface, 3 (2012) 227 (in Russian).
12. *Smith A.L.* Applied Infrared Spectroscopy, John Wiley and Sons, New York, 1979, 658 p.
13. *Bellamy L.J.* Advances in Infrared Group Frequencies, Methuen, London, 1968, 320 p.
14. *Szejtli J.* Introduction and general overview of cyclodextrin chemistry, Chem. Rev., 98 (1998) 1743.
15. *Hedges A.R.* Industrial applications of cyclodextrins, Chem. Rev., 98 (1998) 2035.
16. *Phan T.N.T., Bacquet M., Laureyns J., Morcellet M.* New silica gels functionalized with 2-hydroxy-3-methacryloyloxypropyl- $\beta$ -cyclodextrin using coating or grafting methods, Phys. Chem. Chem. Phys., 1 (1999) 5189.
17. *Gao Z.-W., Zhao X.-P.* Guest-controlling effects on ER behaviors of  $\beta$ -cyclodextrin polymer, J. Colloid Interface Sci., 289 (2005) 56.
18. *Pearson R.G.* Absolute electronegativity and hardness: application to inorganic chemistry, Inorg. Chem., 27 (1988) 734.
19. *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., 92 (1988) 3613.
20. *Pearson R.G.* The theory of soft and hard acids and bases, J. Chem. Educ., 45 (1963) 581.

Received 10.06.2014, accepted 17.09.2014