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PERIODIC MESOPOROUS ORGANOSILICAS WITH CHEMICALLY IMMOBILIZED β-CYCLODEXTRIN MOIETIES FOR BILE SALTS SORPTION

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Mesoporous silicas of MCM-41 type with surface silanol, 3-aminopropyl, and β-cyclodextrin-containing groups were prepared by hydrothermal-assisted base-catalyzed sol-gel condensation of structure-forming silanes in the presence of micelles of long-chain quaternary ammonium salt. Characterization of synthesized silica materials was realized by low-temperature nitrogen adsorption-desorption and chemical analysis of surface layer. It was found that addition of β-cyclodextrin-containing silane into the sol-gel reaction mixture causes formation of MCM-41-type organosilica with higher surface area and hexagonally arranged uniform mesoporous structure. Sorption ability of synthesized silica materials towards sodium cholate and sodium taurocholate was studied in dependence of solution *pH* and concentration. It was found that sorption increases due to chemical immobilization of oligosaccharide moieties in the surface layer of silica, and achieves maximal values in the *pH* regions of molecular forms of bile acids prevailing. Experimental sorption results were analyzed using Freundlich, Redlich – Peterson, and Brunauer – Emmett – Teller models. The formation of island-type structures of bile salts with β-cyclodextrin-containing surface sorption centers due to cooperative interactions between sorbate moieties was proved.

Keywords: sol-gel synthesis; MCM-41; chemical modification; β-cyclodextrin; bile salts sorption.

INTRODUCTION. Bile acids (BAs) are steroid substances with four rings, a five- or eight-carbon side chains terminated with carboxylic group, and hydroxylic groups, whose position and number varies among the acids. The primary BAs (cholic (CA) and chenodeoxycholic) are synthesized from cholesterol in the liver, secreted along with their conjugated glycine or taurine forms into the bile, concentrated in the gallbladder, and released into the upper intestine. Primary BAs are converted to the secondary ones (deoxycholic, lithocholic, and ursodeoxycholic) at bacterial actions in the colon. BAs play the important role as biological surfactants for dietary fats and oils solubilization. They transport in the small bowel

and undergo almost complete reabsorption in the distal ileum with subsequent reuptake from portal blood by the liver [1]. But, the effect of BAs is not restricted by gastrointestinal tract and can involve different tissues throughout the organism. Along with the ability to participate in lipids digestion due to the reduction of the interfacial tension, BAs can serve as signaling molecules influencing metabolic processes [1]. Enterohepatic circulation of BAs affects cholesterol metabolism and plays crucial role in pathogenesis of atherosclerosis. Therefore, development of strategies for precise control of BAs content and cholesterol excretion in the form of neutral sterols or BAs has noticeable importance in treatment of hypercholesterolemia.

Despite of many efforts made in the past decades to improve accuracy and sensitivity of analysis methods or enhance the efficiency of BAs content regulation, design of sorption, separation and detection approaches is still of current interest. Low content of BAs, which varies from micromolar in serum and urine to millimolar in gallbladder bile, and noticeably different physicochemical properties complicate their separation and detection.

Among variety of materials used in BAs sorption silica belongs to the most promising one because of its attractive properties such as large surface area and pore volume, easy surface functionalization, possibility of regeneration. Along with hydroxylated silica gel [2, 3], identification and separation of steroid substances, in particular cholesterol and bile acids, can be realized using impregnated [2, 4] and chemically modified silicas [5, 6]. Combination of contribution from hydrophobic interactions arising between steroid skeleton of BAs and hydrophobic areas of sorbent with geometric complementarity of sorbate and sorption sites on silica surface can be considered as the most suitable approach for creation of highly effective sorbents. Silica surface can gain the ability to recognize steroid substances selectively after chemical immobilization of cyclodextrin (CD) macromolecules. Cyclodextrins (CDs) are cyclic oligosaccharides consisting of D-(+)-glucopyranose units bounded together by α(1→4) linkages. Due to the hydrophilic outer surface and hydrophobic central cavity CDs are able to form water-soluble inclusion complexes with many lipophilic compounds, including cholesterol and BAs, via host-guest interactions. The stability of supramolecular complexes is highly influenced by the polarity of the guest compound and its steric complementarity with CD cavity. It was proved that CDs retain their ability for binding of steroid substances after chemical immobilization into surface layer of silica carrier [7, 8].

In the present work, mesoporous silica nanoparticles (MSNs) of MCM-41 type with surface β-CD-containing groups were prepared by base-catalyzed sol-gel condensation of structure-forming silanes in the presence of cetyltrimethylammonium bromide (CTAB) as template. To identify the *pH* region most suitable for selective recognition of bile salts (BSs) and elucidate the contribution of β-CD-containing sites in sorption efficiency of synthesized materials in the conditions of gastrointestinal tract, sorption of sodium cholate (NaC) and sodium taurocholate (NaTC) was studied in dependence of *pH* value and sorbate concentration.

EXPERIMENT AND DISCUSSIONS OF THE RESULTS. Materials. Tetraethyl orthosilicate (TEOS) (Merck, purity ≥ 99 %), 3-aminopropyltriethoxysilane (APTES) (Merck, purity ≥ 99 %), cetyltrimethylammonium bromide

(Merck, purity ≥ 97 %), 1,1'-carbonyldiimidazole (CDI) (Merck, purity ≥ 98 %), sodium cholate (Frontier Scientific, purity ≥ 98 %), sodium taurocholate (Frontier Scientific, purity ≥ 98 %), aqueous ammonia 25 % (Reakhim, analytical grade), ethanol 96 % (Reakhim, chemical grade), hydrochloric acid 37 % (Reakhim, chemical grade), phosphoric acid 85 % (Reakhim, analytical grade), sulfuric acid 98 % (Reakhim, chemical grade), disubstituted sodium phosphate (Reakhim, analytical grade), and monosubstituted potassium phosphate (Reakhim, analytical grade), sodium carbonate (Reakhim, analytical grade), sodium hydroxide (Reakhim, analytical grade), potassium ferricyanide (Reakhim, analytical grade), glucose (Reakhim, analytical grade) were employed without preliminary purification. β-Cyclodextrin (Fluka, purity ≥ 99 %) was used after drying in an oven at 373 K for 2 h. N,N′-dimethylformamide (DMF) (Reakhim, analytical grade) was dried by activated NaA molecular sieves for 24 h.

Sol-gel synthesis of mesoporous silica materials. The high-quality mesoporous silicas of MCM-41 type were prepared by hydrothermal-assisted base-catalyzed sol-gel condensation of structure-forming silanes in the presence of micelles of long-chain quaternary ammonium salt as structure directing agents. Molar compositions of the initial gel reaction mixtures at synthesis of silica materials are represented in Table 1.

Table 1.

Molar compositions of reaction mixtures at synthesis of silica materials.

Silica	Molar composition of reaction mixture
MSN-C_{16}	0.1 TEOS : 0.02 CTAB : 0.54 NH_4OH : 0.56 C_2H_5OH : 14.4 H_2O
NH_2-MSN-C_{16}	0.096 TEOS : 0.004 APTES : 0.012 CTAB : 0.54 NH_4OH : 14.4 H_2O
CD-NH_2-MSN-C_{16}	0.098 TEOS : 0.002 β-CD-silane : 0.012 CTAB : 0.54 NH_4OH : 14.4 H_2O

MSNs with surface silanol and 3-aminopropyl groups were synthesized using CTAB as pore-forming agent (Table 1). For this, the batch of CTAB was placed into a conical vessel and dissolved in mixture of deionized water and ethanol. After that, 25 % aqueous ammonium solution was poured into the reaction vessel and TEOS or its mixture with APTES was slowly added during 15 min under vigorous stirring. The resultant reaction slurry was stirred at 293 K for 2 h, then transferred into a polypropylene bottle and aged at 373 K without stirring for 24 h. After hydrothermal treatment synthesized MSN-C_{16} and NH_2-MSN-C_{16} silicas were filtered, washed with deionized water and dried in air at 373 K for 2 h.

Silica material of MCM-41-type with chemically immobilized β-CD-containing moieties was synthesized according to the described earlier procedures using β-CD-silane along with TEOS as silica source (Table 1). For β-CD-silane synthesis, the batch of β-CD was dissolved in minimal volume of DMF and treated with equimolar quantity of CDI (taken with 5% excess) dissolved in DMF at 293 K for 2 h. Then, equimolar quantity of APTES was added into the reaction flask at continuous stirring to link with activated oligosaccharide. The solution

was stirred at 293 K for 20 h and used for sol-gel synthesis of CD-NH_2-MSN-C_{16} silica.

Removal of long-chain quaternary ammonium salt from the pore volume of mesoporous silicas was realized by extraction in acid-ethanol medium. Briefly, the batch of the as-synthesized material (1 g) was stirred with a solution of hydrochloric acid (8 ml) and ethanol (92 ml) at 293 K for 24 h. After separation of silica particles from solution by filtration the extraction procedure was repeated two more times. The resulting mesoporous silica was filtered, washed with deionized water until the absence of halogen ions in filtrate (negative probe with silver nitrate), and dried in the air at 373 K for 5 h.

Characterization of mesoporous silica materials. Nitrogen adsorption-desorption isotherms were measured at 77 K with a Kelvin-1042 Sorptometer. Prior to the analysis, silica materials were outgassed under vacuum at 413 K for 20 h. The values of Brunauer – Emmett – Teller (BET) specific surface area were calculated using adsorption data registered in the region of relative pressures from 0.06 to 0.99 in increment of 0.015. The pore size distribution curves were obtained from analysis of the adsorption branch of the isotherms by density functional theory (DFT) algorithm. The total pore volumes of synthesized MSNs were determined from the amount of adsorbed nitrogen at a relative pressure of about 0.99.

The content of surface 3-aminopropyl groups was determined from the results of the potentiometric titration with 0.01 M HCl. Briefly, the batch of mesoporous organosilica (0.5 g) was placed into a volumetric flask and poured with 0.01 M HCl (25 ml). The resulting suspension was stirred at 294 K for 24 h to attain equilibrium. *pH* of starting and equilibrium solutions were measured by an Ionometer I–120.1. The content of 3-aminopropyl groups chemically immobilized on silica surface was calculated by the equation:

$$C_{NH_2} = \frac{(10^{-pH_1} - 10^{-pH_2}) \cdot V}{m}, \qquad (1)$$

where C_{NH_2} is the content of 3-aminopropyl groups of silica, mol·g^{-1}; pH_1 and pH_2 are the *pH* of starting and equilibrium solutions, correspondingly; V is the volume of solution, l; m is the batch of silica, g.

The content of β-CD moieties introduced into the MSNs at the process of sol-gel synthesis was estimated by acid hydrolysis of surface β-CD-containing groups to glucose. For this, the batch of silica (0.1 g) was refluxed with 1 M H_2SO_4 (15 ml) at 373 K for 2 h. Then, the solution was neutralized with 5 M NaOH up to *pH* 7, filtered, and diluted up to 50 ml with water. Aliquot of this solution (2 ml) was held in the boiling flask with of 0.05 % $K_3Fe(CN)_6$ (25 ml) dissolved in 1 % Na_2CO_3 water solution at 373 K for 10 min. On cooling concentration of glucose was determined as its coloured complex with potassium ferricyanide from the value of optical density of the absorption band at λ = 420 nm. The glucose calibration curve was plotted over the range 0–0.888 mmol·l^{-1}. Content of grafted β-CD was calculated by the equation:

$$[\beta\text{-}CD] = \frac{C \cdot V}{7 \cdot m}, \qquad (2)$$

where *[β-CD]* is the content of β-CD on the silica surface, mmol·g^{-1}; C is the concentration of glucose in the solution, mmol·l^{-1}; V is the volume of solution, l; m is the batch of β-CD-containing silica, g.

Sorption studies. UV-Vis spectra of BSs in phosphate buffer solutions (PBSs) were

recorded in 200–600 nm spectral range with a Specord M-40 using quarts cells with 5 mm path length. All spectroscopic measurements were made with temperature-controlled cell holder and water bath. *pH* of solutions were measured by an Ionometer I–120.1 that was calibrated for optimal precision using standard buffer solutions.

Sorption of BSs on synthesized mesoporous silica materials in dependence of *pH* was carried out from 0.18 mmol·l^{-1} solutions in PBS. Briefly, batches of silicas (0.02 g) were placed in 50 ml glass beakers and solutions of BSs in PBSs (10 ml) with predetermined *pH* in the range from 1.0 to 8.0 were added. Prepared suspensions were shaken at 297 K for equilibrium attainment. Supernatant solutions were separated by filtering through a 0.22 μm PVDF syringe filter, treated with concentrated sulfuric acid to obtain coloured complex [9] and analyzed at λ = 389 nm. The amount of NaC or NaTC sorbed on silica surface was calculated using calibration curves plotted for each *pH* value by the equation:

$$A = \frac{(C_o - C_{eq}) \cdot V}{m \cdot S_{BET}}, \qquad (3)$$

where *A* is the content of BS sorbed on silica surface at equilibrium, mmol·m^{-2}; C_o and C_{eq} are the concentrations of BS at initial moment and at equilibrium, correspondingly, mmol·l^{-1}; *V* is the volume of solution, l; m is the batch of silica, g; S_{BET} is the specific surface area of silica, m^2·g^{-1}.

Equilibrium sorption of BSs on synthesized MSNs was studied from 0.06–0.3 mmol·l^{-1} solutions with *pH* 5.0 and 7.4 as described above for sorption in dependence of *pH*.

Sorbents characterization. Low-temperature nitrogen adsorption-desorption isotherm of MSN-C_{16} silica is represented in Figure 1. The profile of MSN-C_{16} isotherm belongs to the type IV with hysteresis loop of the type H4 as defined by IUPAC classification (Fig. 1). According to the pore size distribution plot calculated by the DFT model, formation of silica framework with two prevailing pore diameters takes place (Fig. 2, Table 2).

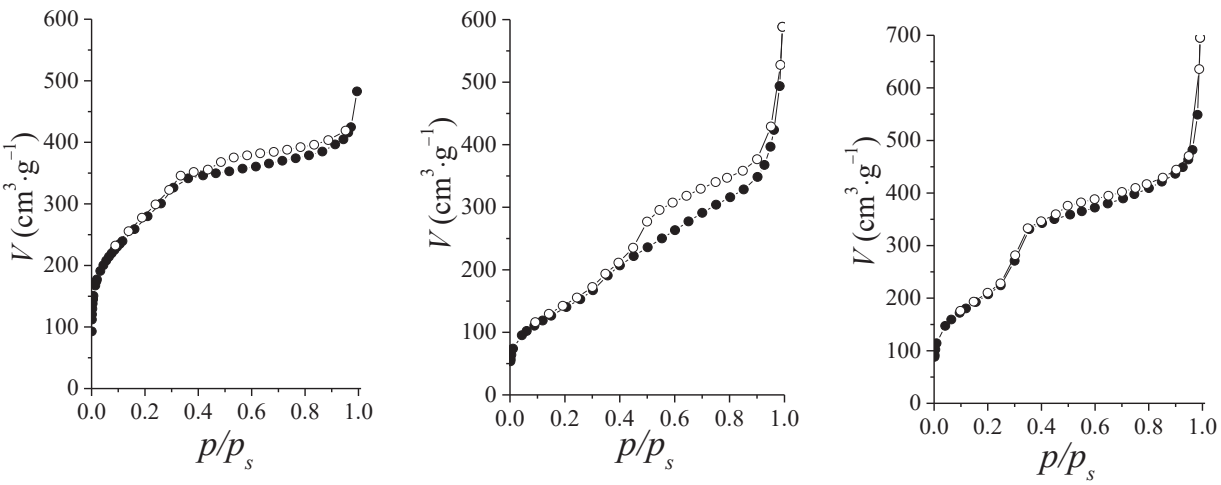


Fig. 1. Isotherms of low-temperature nitrogen adsorption-desorption on MSN-C_{16} (a), NH_2-MSN-C_{16} (b), and CD-NH_2-MSN-C_{16} (c).

Addition of APTES in sol-gel reaction mixture has noticeable influence on structural parameters of resulting NH_2-MSN-C_{16} material. Transformation of isotherm into the type IV with hysteresis loop of the type H3 is observed. As can be seen from the pore size distribution curve, mesopore diameter controlled by CTAB template is prevailing (Figs. 2, Table 2). It should be mentioned that increase of mesopores size is observed (Table 2). Obviously, porous structure of synthesized material is predetermined not only by the long-chain alkyltrimethyl ammonium salt as structure directing agent but in the great extent by the presence of functional silane, which functionalities interact with template and participate in condensation process.

Introduction of β-CD-silane, obtained by coupling of oligosaccharide with equimolar quantity of APTES, in reaction mixture of sol-gel synthesis causes formation of CD-NH_2-MSN-C_{16} material with higher surface area in comparison with NH_2-MSN-C_{16} (Table 2). Moreover, it should be mentioned, that the profiles of low-temperature nitrogen adsorption-desorption isotherm obtained for CD-NH_2-MSN-C_{16} is similar to that one for MSN-C_{16} (Fig. 1). Analysis of pore size distribution curve proves that addition of β-CD-silane as structure-forming agent in sol-gel reaction mixture results in organosilica with homogeneous mesoporosity (Figs. 2, Table 2). Thus, β-CD-silane has positive impact on structural characteristics of synthesized CD-NH_2-MSN-C_{16} material.

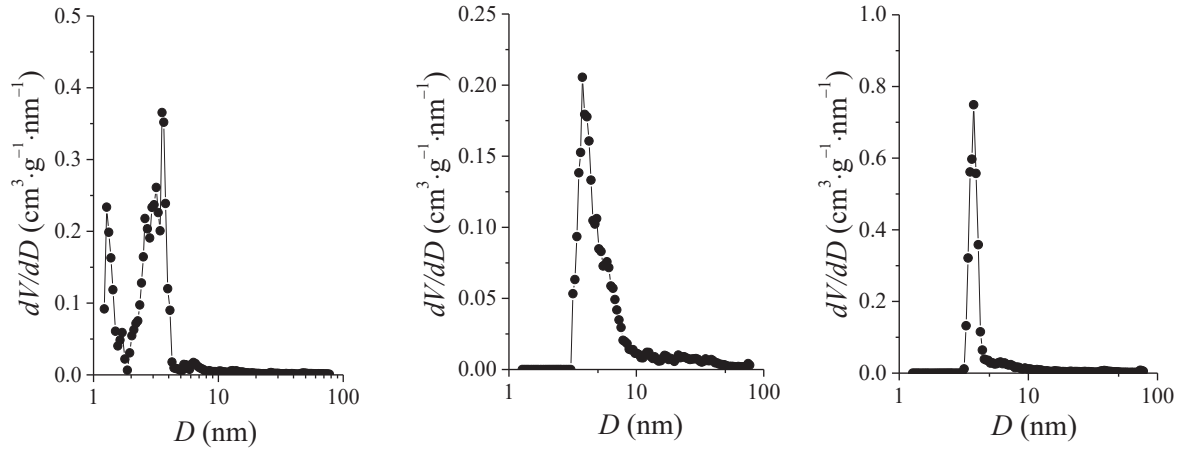


Fig. 2. Pore size distribution in MSN-C_{16} (a), NH_2-MSN-C_{16} (b), and CD-NH_2-MSN-C_{16} (c).

Table 2.

Structural characteristics of MCM-41-type silicas.

Silica	Low-temperature nitrogen adsorption-desorption			Chemical analysis of surface layer			
				[NH_2]		*[β-CD]*	
	S_{BET}, $m^2 \cdot g^{-1}$	*V*, $cm^3 \cdot g^{-1}$	*D*, nm	$mmol \cdot g^{-1}$	$\mu mol \cdot m^{-2}$	$mmol \cdot g^{-1}$	$\mu mol \cdot m^{-2}$
MSN-C_{16}	995	0.75	1.27; 3.54	–	–	–	–
NH_2-MSN-C_{16}	515	0.91	3.78	0.28	0.54	–	–
CD-NH_2-MSN-C_{16}	758	1.08	3.78	0.34	0.45	0.029	0.038

Sorption of bile salts by mesoporous silica materials. The effect of the solution acidity on the sorption of BSs by synthesized MSNs was studied in PBSs with predetermined *pH* in the range from 1.0 to 8.0 (Fig. 3). It was found that sorption of NaC by MSNs with surface silanol and 3-aminopropyl groups is insufficient (Fig. 3).

The profiles of NaTC sorption curves on MSNs differ from that ones obtained for NaC (Fig. 3). Slight decrease of MSN-C_{16} and NH_2-MSN-C_{16} sorption is observed in acidic medium. Obviously, this is related with the difference in physico-chemical characteristics reflecting protolytic (acid ionization constant K_a) and hydrophobic/hydrophilic properties (critical micelle concentration CMC, octanol-water partition coefficient $P_{o/w}$) of BSs (Table 3).

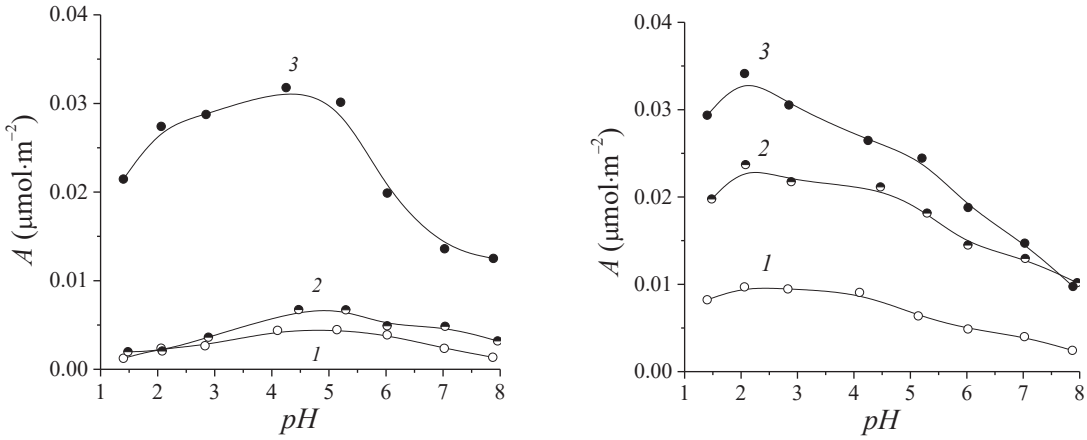
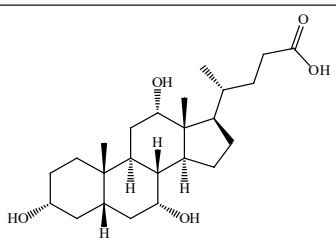
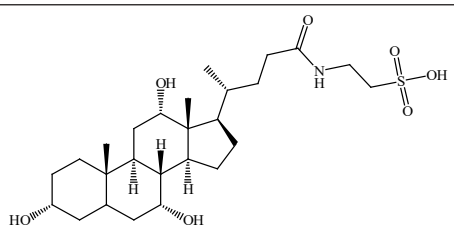


Fig. 3. Effect of *pH* on NaC (a) and NaTC (b) sorption by MSN-C_{16} (curve *1*), NH_2-MSN-C_{16} (curve *2*), and CD-NH_2-MSN-C_{16} (curve *3*) from PBSs at 297 K.

Table 3.

Physico-chemical parameters of bile acids.

Bile acid	Structure	pK_a [10]	CMC, mmol·l^{-1} [11]	log $P_{o/w}$ (HBA) [12]	log $P_{o/w}$ (BA^-) [12]
CA		4.6	11–13	2.02	1.1
TCA		1.4	6–10	not determinable	–0.50

Lower values of CMC and octanol-water partition coefficients for molecular and dissociated species of conjugated TCA in comparison with unconjugated CA indicates its less pronounced tendency to self-association and higher affinity to hydrophilic surface groups of sorbent. At the same time, conjugation of CA with taurine reduces the pK_a value and enhances solubility of product in aqueous medium drastically. So, contrary to the CA, for which molecular protolytic form is predominant below *pH* 4.6, negatively charged dissociated form of TCA is prevailing in all studied *pH* range. Analysis of the effect of *pH* on BSs sorption in the context of protolytic properties of sorbate and sorbent evidences that increase of NaC and NaTC sorption by MSN-C_{16} and NH_2-MSN-C_{16} is mainly associated with hydrogen bonds formation and electrostatic interactions between non-ionized silanol (pK_a = 6.9) and protonated 3-aminopropyl groups (pK_a = 3.8) of silica surface, correspondingly, and anionic forms of BAs (Fig. 3). Further accumulation of bile acids anions in solution and negatively charged functional groups on silica surface at $pH > 5$ causes reduction in their sorption on MSN-C_{16} and NH_2-MSN-C_{16} as the result of electrostatic repulsion arising between negatively charged sorbate and silica surface (Fig. 3).

Chemical immobilization of β-CD-containing moieties in the surface layer of MCM-41-type silica results in noticeable increase of BSs sorption on CD-NH_2-MSN-C_{16} in comparison with parent materials (Fig. 3). It can be related with the formation of inclusion complexes between surface β-CD-containing groups and molecular or anionic forms of BSs supplied from solution. As seen from Figure 3, NaC and NaTC sorption on β-CD-containing MSNs in dependence of solution *pH* differ noticeably. Contribution of surface supramolecular complexes formation in total NaC sorption on CD-NH_2-MSN-C_{16} is more pronounced in acidic medium than in neutral one. Obviously, cholate anions, which prevail in a solution with *pH* exceeding pK_a (Table 3), form weaker surface inclusion complexes with β-CD-containing groups as theirs localization in the β-CD cavity is less favorable due to the lower hydrophobicity in comparison with molecular form of CA. Decrease of NaTC sorption on CD-NH_2-MSN-C_{16} begins at much lower *pH* values than for NaC (Fig. 3). Such differences in *pH*-dependent curves are due to the appearance and accumulation of taurocholate anions in strongly acidic medium.

It should be pointed out that substantial difference in sorption of NaC and NaTC by β-CD-containing silicas, which is observed at *pH*~2, gradually decreases with *pH* rise. So, the ability of CD-NH_2-MSN-C_{16} silica for selective sorption of BSs can be considered only in highly acidic medium and reduces significantly at *pH* values from 4 to 8 (Fig. 3). This phenomenon can be clarified by comparison of inclusion complexes formation on silica surface with that ones in a solution. Quantitative estimation of "β-CD–BS" inclusion complexes stability in solutions by means of isothermal calorimetric and spectroscopic titrations as well as ^{1}H-NMR and ^{13}C-NMR measurements was realized by authors [13, 14]. The maximal sorption efficiency of BSs by MSNs, which is achieved in the *pH* range from 4 to 5 for NaC and at *pH* 2 for NaTC, is predetermined by their protolytic properties and formation of stable supramolecular inclusion complexes. Whereas, the absence of drastic difference in sorption ability of β-CD-containing silica material towards NaC and NaTC in neutral

medium is in a good agreement with the experimental results obtained for inclusion complexes of BSs with β-CD in PBS, according to which the same order of stability constant values was observed.

In the human small intestine, the *pH* level varies from 4.0 to 8.3. The mean *pH* in the proximal small intestine consists of 6.6, whereas in the terminal ileum it equals to 7.5. Although the highest values of BSs sorption were achieved in weakly acidic and acidic medium for NaC and NaTC, correspondingly, the sorption studies were performed at *pH* 5.0 (BAs are present in different protolytic forms) and *pH* 7.4 (both BAs are fully dissociated), to provide useful information for simulation of BSs sorption in the gastrointestinal tract.

As seen from the experimental data obtained for BSs sorption on MSNs, isotherms have different shape reflecting influence of sorbate and sorbent nature and affinity arising between them on sorption process (Figs. 4, 5). Extremely low values of BSs sorption by MSN-C_{16} and NH_2-MSN-C_{16} at concentrations up to 0.17 mmol·l^{-1} is indicative of weak sorbate-sorbent interactions at *pH* 5 and 7.4 (Fig. 4, 5). Increase of NaC and NaTC concentrations results in gradual rise of isotherms. This phenomenon may be caused by cooperative interactions of BSs sorbed on silica surface with that ones supplied from solution (Figs. 4, 5).

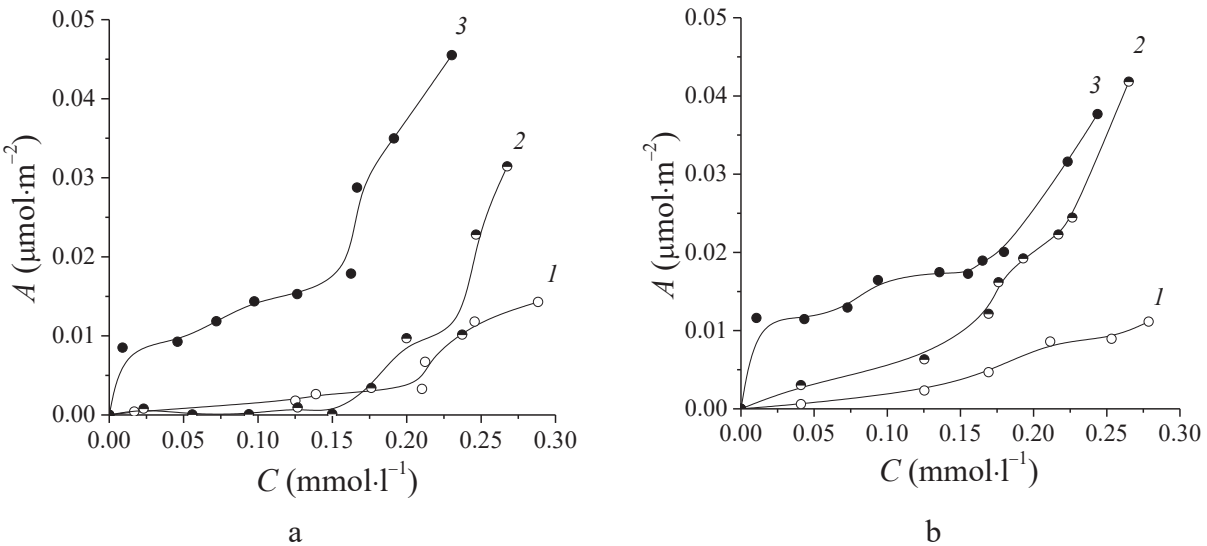


Fig. 4. Isotherms of NaC (a) and NaTC (b) sorption by MSN-C_{16} (curve *1*), NH_2-MSN-C_{16} (curve *2*), and CD-NH_2-MSN-C_{16} (curve *3*) from PBSs with *pH* 5.0 at 297 K.

CD-NH_2-MSN-C_{16} demonstrates enhanced affinity to sorbate at both studied *pH* values. Complexity in structure of surface layer of CD-NH_2-MSN-C_{16} in comparison with parent silica materials causes substantial changes in the profiles of BSs sorption curves (Figs. 4, 5). Noticeable enhancement of BSs sorption by MSNs with chemically immobilized oligosaccharide moieties begins in the region of small concentrations of sorbate and acquires rapid

growth above 0.2 mmol·l^{-1} (Figs. 4, 5). It can be attributed to the formation of inclusion complexes with participation of surface β-CD-containing groups reinforced by cooperative interactions of sorbed BSs with supplied from solution ones. Thus, even negatively charged cholate and taurocholate anions, which prevail in solution at *pH* 7.4, participate in surface inclusion complexes formation and make noticeable contribution to the total sorption on CD-NH_2-MSN-C_{16}. It should be noted that NaC sorption on CD-NH_2-MSN-C_{16} is slightly higher than that of NaTC. It can be explained by the differences in BSs structure and physico-chemical properties (Table 3).

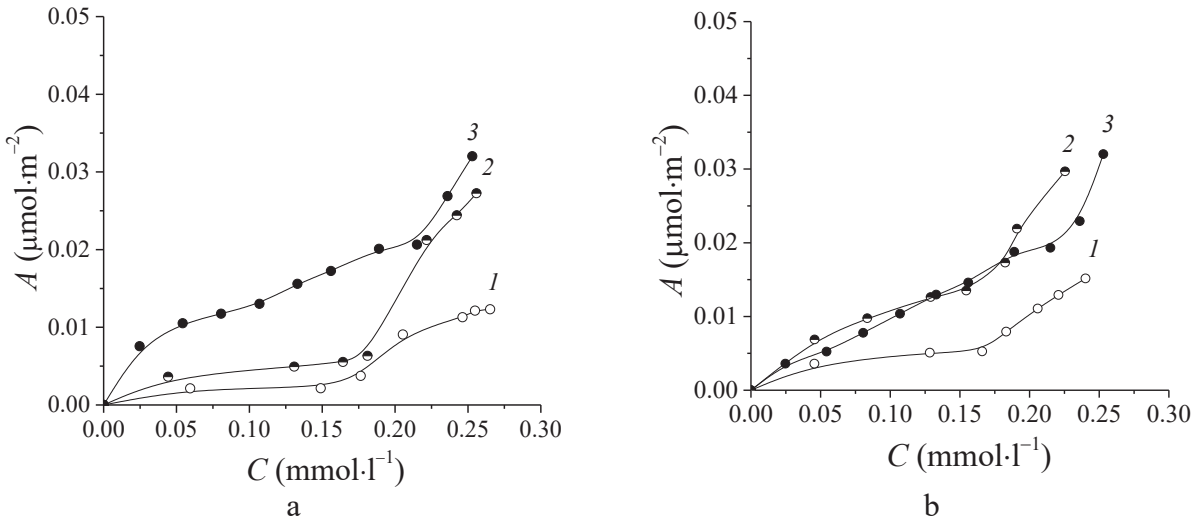


Figure 5. Isotherms of NaC (a) and NaTC (b) sorption by MSN-C_{16} (curve *1*), NH_2-MSN-C_{16} (curve *2*), and CD-NH_2-MSN-C_{16} (curve *3*) from PBSs with *pH* 7.4 at 297 K.

The experimental isotherms were analyzed using Freundlich, Redlich – Peterson, and Brunauer – Emmett – Teller (BET) equations. The Freundlich isotherm theory describes monolayer sorption on heterogeneous surface with energetically non-equivalent sorption sites. Redlich – Peterson model can predict sorption either on heterogeneous or homogenous sites of silica surface for which the mechanism of sorption has hybrid character. The modified BET isotherm equation for multilayer sorption from liquid phase assumes that solvent is weakly sorbed on silica surface.

To find out the isotherm model that can describe experimental sorption isotherms in the best way and give precise values of equilibrium sorption parameters, analysis of the linear form of Freundlich equation or nonlinear regression analysis of Redlich – Peterson and BET equations was realized (Tables 4–7). Estimated statistical error function, the correlation coefficient (R^2), of linearized Freundlich model is significantly lower compared to that ones obtained at non-linear modeling of experimental results with Redlich – Peterson and BET equations.

Table 4.

Parameters of BSs sorption on MSNs at *pH* 5.0 (the Freundlich and Redlich – Peterson models).

Equilibrium sorption model		Freundlich			Redlich – Peterson				
Linear form of equation		$lg\,A_{eq} = lg\,K_F + \frac{1}{n} lg\,C_{eq}$			$A_{eq} = \frac{K_R C_{eq}}{1 + a_R C_{eq}^{\beta}}$				
Sorption parameters		K_F	n	R^2	K_R	a_R	β	R^2	χ^2
NaC	MSN-C_{16}	0.035	0.876	0.915	0.036	0.002	$4.6 \cdot 10^{-13}$	0.719	11.136
	NH_2-MSN-C_{16}	0.091	0.505	0.646	0.061	$6.674 \cdot 10^{-4}$	$1 \cdot 10^{-12}$	0.529	17.849
	CD-NH_2-MSN-C_{16}	0.055	2.112	0.811	0.167	$3.9 \cdot 10^{-17}$	0.01	0.862	19.312
NaTC	MSN-C_{16}	0.077	0.645	0.989	0.036	$1.7 \cdot 10^{-15}$	0.01	0.918	2.397
	NH_2-MSN-C_{16}	0.166	0.751	0.943	0.130	0.191	$1 \cdot 10^{-16}$	0.790	0.790
	CD-NH_2-MSN-C_{16}	0.038	3.086	0.784	$7.97 \cdot 10^{3}$	$9.41 \cdot 10^{4}$	0.279	0.797	14.758

A_{eq} – amount of BS sorbed on silica surface, μmol·m^{-2}; C_{eq} – concentration of BS in the solution after equilibrium attainment, mmol/l; K_F – the Freundlich constant that indicates the extent of surface heterogeneity, 1·m^{-2}; *1/n* – measure of sorption intensity, which can be between 0 and 1; K_R and a_R – the Redlich – Peterson isotherm constants, l·m^{-2} and l·mmol^{-1}, correspondingly; β – exponent that lies between 0 and 1

Table 5.

Parameters of BSs sorption on MSNs at *pH* 7.4 (the Freundlich and Redlich – Peterson models).

Equilibrium sorption model		Freundlich			Redlich – Peterson				
Linear form of equation		$lg\,A_{eq} = lg\,K_F + \frac{1}{n} lg\,C_{eq}$			$A_{eq} = \frac{K_R C_{eq}}{1 + a_R C_{eq}^{\beta}}$				
Sorption parameters		K_F	n	R^2	K_R	a_R	β	R^2	χ^2
NaC	MSN-C_{16}	0.055	0.777	0.835	0.046	0.124	$1 \cdot 10^{-14}$	0.810	6.866
	NH_2-MSN-C_{16}	0.077	0.897	0.784	0.091	0.127	$1 \cdot 10^{-16}$	0.705	12.656
	CD-NH_2-MSN-C_{16}	0.054	1.762	0.953	$3.32 \cdot 10^{3}$	$4.244 \cdot 10^{4}$	0.234	0.929	4.069
NaTC	MSN-C_{16}	0.035	1.251	0.847	0.053	0.023	$1 \cdot 10^{-16}$	0.852	5.382
	NH_2-MSN-C_{16}	0.077	1.212	0.941	0.110	$4.021 \cdot 10^{-6}$	$4.1 \cdot 10^{-9}$	0.914	2.684
	CD-NH_2-MSN-C_{16}	0.084	1.108	0.980	0.113	0.096	$1 \cdot 10^{-16}$	0.943	3.624

Table 6.

Parameters of BSs equilibrium sorption on MSNs at *pH* 5.0 (the Brunauer – Emmett – Teller model).

Equilibrium sorption model		Brunauer – Emmett – Teller				
Equation		$A_{eq} = \frac{A_m K_S C_{eq}}{(1 - K_L C_{eq})(1 - K_L C_{eq} + K_S C_{eq})}$				
Parameters		K_S	K_L	A_m	R^2	χ^2
NaC	MSN-C_{16}	0.049	1.957	0.207	0.919	3.213
	NH_2-MSN-C_{16}	0.089	3.787	0.016	0.999	0.003
	CD-NH_2-MSN-C_{16}	220.217	3.379	0.01	0.941	8.262
NaTC	MSN-C_{16}	0.028	1.110	0.708	0.967	0.974
	NH_2-MSN-C_{16}	2.832	2.772	0.014	0.989	0.597
	CD-NH_2-MSN-C_{16}	$2.923 \cdot 10^6$	2.898	0.01	1	$3.228 \cdot 10^{-4}$

K_S – term for the energy of interaction with the surface, l·mmol^{-1}; K_L – equilibrium constant for surface sorption-desorption, l·mmol^{-1}.

Table 7.

Parameters of BSs sorption on MSNs at *pH* 7.4 (the Brunauer – Emmett – Teller model).

Equilibrium sorption model		Brunauer – Emmett –Teller				
Equation		$A_{eq} = \frac{A_m K_S C_{eq}}{(1 - K_L C_{eq})(1 - K_L C_{eq} + K_S C_{eq})}$				
Parameters		K_S	K_L	A_m	R^2	χ^2
NaC	MSN-C_{16}	0.021	1.816	0.638	0.939	2.214
	NH_2-MSN-C_{16}	0.059	2.414	0.290	0.946	2.299
	CD-NH_2-MSN-C_{16}	120.785	2.721	0.009	0.988	0.662
NaTC	MSN-C_{16}	$1.152 \cdot 10^7$	3.442	0.003	1	$2.904 \cdot 10^{-4}$
	NH_2-MSN-C_{16}	82.704	3.360	0.007	0.988	0.368
	CD-NH_2-MSN-C_{16}	23.635	2.855	0.009	0.979	1.318

High R^2 values obtained for Freundlich model clearly indicates a pronounced heterogeneous nature of BSs sorption on MSNs. Whereas, close values of the correlation coefficients estimated by Redlich-Peterson and BET models prove ambiguous nature of BSs sorption on synthesized silica materials due to the hydrogen bonds formation or electrostatic interactions between different surface functional groups of silica sorbents and BSs as well as surface inclusion complexes formation followed by stacking of sorbed moieties of BSs and supplied from solution ones. In most cases, the highest values of correlation coefficients were obtained at applying of BET model to the isotherms of BSs sorption on MSNs (Tables 6, 7). To ensure the suitability of BET model for precise description of experimental sorption isotherms, the results of Chi square test (χ^2) were analyzed. According to the data represented in Tables 4–7, application of BET theory gives smaller χ^2 values than modelling of experimental isotherms with Redlich-Peterson equation. So, an assessment of statistical error functions proves that the best fit for BSs sorption process on MSNs is attained at BET model application. It can be assumed that sorption of BSs proceeds due to the formation of island-type supramolecular structures with β-CD-containing surface centers in which cooperative interactions play crucial role. Comparison of sorption data calculated by BET model with experimental ones is represented in Figures 6, 7.

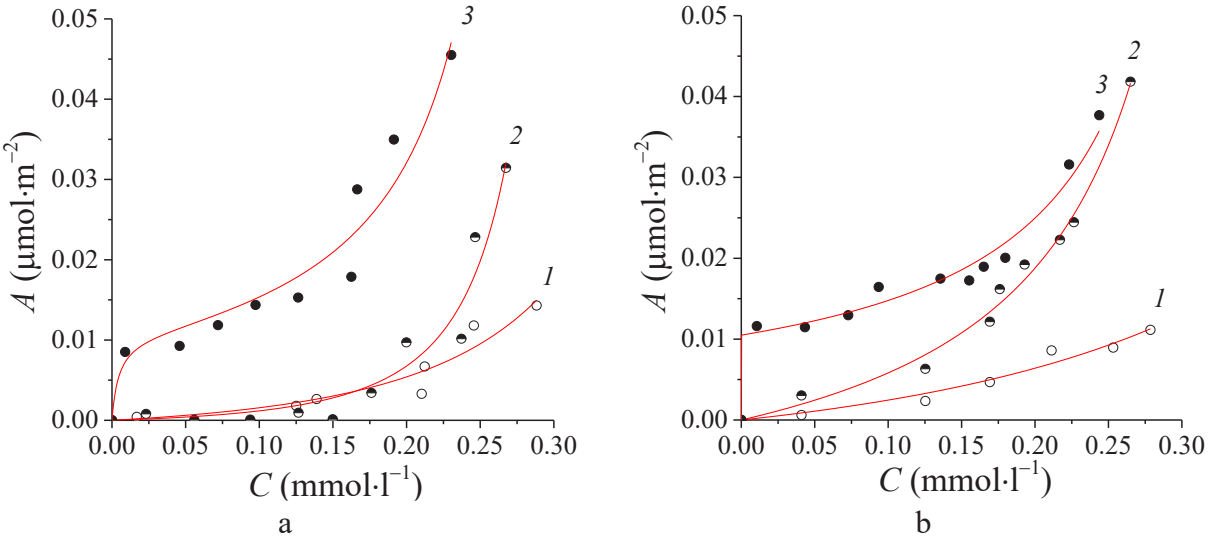


Fig. 6. Isotherms of NaC (a) and NaTC (b) sorption by MSN-C_{16} (curve *1*), NH_2-MSN-C_{16} (curve *2*), and CD-NH_2-MSN-C_{16}(curve *3*) from PBSs with *pH* 5.0 calculated by nonlinear regression analysis of BET equation.

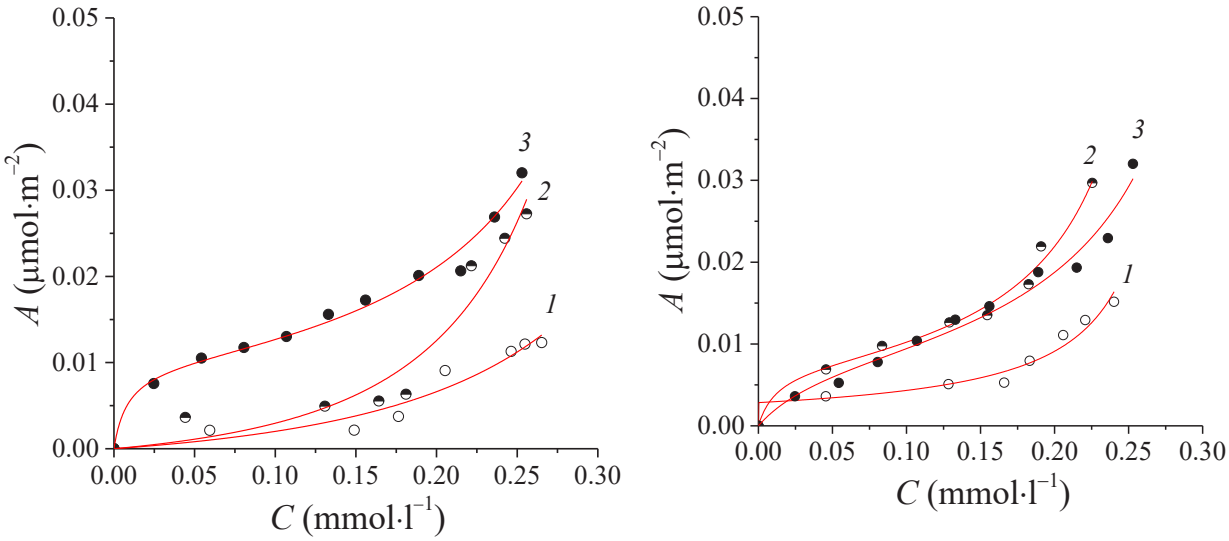


Fig. 7. Isotherms of NaC (a) and NaTC (b) sorption by MSN-C_{16} (curve *1*), NH_2-MSN-C_{16} (curve *2*), and CD-NH_2-MSN-C_{16} (curve *3*) from PBSs with *pH* 7.4 calculated by nonlinear regression analysis of BET equation

CONCLUSIONS. In the present paper, sorption of NaC and NaTC by periodic mesoporous organosilicas with chemically immobilized β-CD was studied. It was established that introduction of oligosaccharide moieties in surface layer of silica sorbent leads to the substantial enhancement of BSs sorption. The most pronounced difference in NaC and NaTC sorption was registered in highly acidic medium (*pH*~2) with different protolytic forms of BAs. Substantial increase of *pH* leads to the accumulation of cholate and taurocholate anions in solution and causes convergence of NaC and NaTC sorption values. Slight prevailing of NaC sorption on CD-NH_2-MSN-C_{16} in comparison with NaTC which is observed at *pH* 5 and 7 was explained by differences in surface inclusion complexes stability. Sorption of BSs on synthesized silica materials was analyzed using Freundlich, Redlich-Peterson, and BET models. An assessment of statistical error functions showed that the best fit for BSs sorption process is attained at BET model application. Obtained results let us assume formation of island-type supramolecular structures of BSs with β-CD-containing surface sorption centers in PBSs with *pH* 5.0 and 7.4.

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ВПОРЯДКОВАНІ МЕЗОПОРИСТІ ОРГАНОКРЕМНЕЗЕМИ З ХІМІЧНО ІММОБІЛІЗОВАНИМ β-ЦИКЛОДЕКСТРИНОМ ДЛЯ СОРБЦІЇ СОЛЕЙ ЖОВЧНИХ КИСЛОТ

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Одержано мезопористі органокремнеземи типу МСМ-41 з поверхневими силанольними, 3-амінопропільними та β-циклодекстринвмісними групами золь-гель-конденсацією структуроутворюючих силанів у присутності міцел довголанцюгової четвертинної амонієвої солі за умов лужного каталізу та подальшого гідротермального оброблення. Синтезовані кремнеземні матеріали охарактеризовано з використанням методів низькотемпературної адсорбції-десорбції азоту та хімічного аналізу поверхневого шару. Показано, що додавання β-циклодекстринвмісного силану у реакційну суміш зумовлює формування кремнезему типу МСМ-41 із більшою питомою поверхнею та гексагонально впорядкованою однорідною мезопористою структурою. Сорбційну здатність синтезованих кремнеземних матеріалів відносно холату та таурохолату натрію було вивчено залежно від pH розчину та його концентрації. Встановлено, що сорбція зростає завдяки хімічній іммобілізації олігосахаридних груп у поверхневому шарі кремнезему та досягає максимальних значень у діапазонах pH, де переважають молекулярні форми жовчних кислот. Експериментально одержані результати сорбції проаналізовано з використанням моделей Фрейндліха, Редліха – Петерсона та Брунауера – Еммета – Теллера. Доведено формування структур острівкового типу солей жовчних кислот з β-циклодекстринвмісними поверхневими сорбційними центрами завдяки кооперативним взаємодіям між молекулами сорбату.

Ключові слова: золь-гель-синтез; МСМ-41; хімічне модифікування; β-циклодекстрин; сорбція солей жовчних кислот.

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