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## **$\beta$ -CYCLODEXTRIN-MCM-41 SILICA AS PROMISING ADSORBENT FOR THE TRACE AMOUNTS REMOVAL OF AROMATICS FROM WATER**

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*Aromatic compounds are organic contaminants in aqueous streams of various industries. Even at low concentration, benzene and its derivatives are toxic agents. Silicas are promising materials for benzene and phenol adsorption from water mixtures due to their unique physical and chemical properties. In this research, we realized sol-gel synthesis of  $\beta$ -cyclodextrin-MCM-41 silica using  $\beta$ -cyclodextrin-containing silane and tetraethyl orthosilicate as silica sources in the presence of ionic template (cetyltrimethylammonium bromide).  $\beta$ -Cyclodextrin-silane was prepared by modification of (3-aminopropyl)triethoxysilane with oligosaccharide activated by *N,N'*-carbonyldiimidazole. The successful incorporation of  $\beta$ -cyclodextrin moieties in silica is verified by means of FT-IR spectroscopy and quantitative chemical analysis. Obtained  $\beta$ -cyclodextrin-MCM-41 silica was characterized by X-ray diffraction, transmission electron microscopy, and low-temperature adsorption-desorption of nitrogen. On the basis of analysis,  $\beta$ -cyclodextrin-MCM-41 silica is well-ordered mesoporous material with high surface area (about  $800 \text{ m}^2 \cdot \text{g}^{-1}$ ) and sufficient oligosaccharide group loading (up to  $0.022 \mu\text{mol} \cdot \text{m}^{-2}$ ). Adsorption of benzene and phenol from aqueous solutions on  $\beta$ -cyclodextrin-MCM-41 silica was studied as the function of time and equilibrium concentration. Greater specificity of aromatic compounds adsorption for  $\beta$ -cyclodextrin-MCM-41 silica in comparison with MCM-41 was demonstrated. Moreover, the higher adsorption performance of  $\beta$ -cyclodextrin-MCM-41 silica towards benzene and their adsorptive affinity to phenol can be useful in the separation of aromatic compounds. The proposed synthesis approach may be applicable for obtaining of ordered  $\beta$ -cyclodextrin-containing functional materials with high affinity to aromatic compounds of suitable geometry for water treatment.*

**Keywords:** MCM-41,  $\beta$ -cyclodextrin, sol-gel synthesis, adsorption, aromatic compounds

### INTRODUCTION

Aromatic compounds are organic contaminants in aqueous streams of various industries from production of resin and plastic, leather, paper, synthetic dyes, solvents, pesticides as well as coal conversion and petroleum refining [1]. The widespread using of these chemicals in industry processes also can lead to the presence of aromatic compounds in aquatic environment and drinking water since they exhibit high volatility and spreading as well as low biodegradability. Even at low concentration, benzene and its derivatives are flammable, toxic, carcinogenic, and/or mutagenic agents [2, 3]. There are a variety of chemical and physical methods that have been suggested for the purification of wastewaters from aromatics. Among them the common used are adsorption [4–15], bio- and photodegradation [16, 17], solvent/surfactant extraction [18, 19], chemical oxidation [20], membrane treatment [21], and coagulation-flocculation [22]. However, adsorption has been shown to be one of the most effective procedures in the elimination of benzene

and its derivatives from aqueous solutions. A number of adsorbents were used for benzene and phenol adsorption from water mixtures, such as activated carbons [4–6], zeolites [7, 8], ceramic and polymeric materials [9–13], and bioadsorbents [14, 15]. Even taking into account the advantages of these adsorbents, their potential application is often limited by the cost of material, the low efficiency at trace concentration of analytes, and the necessity of sorbent regeneration at high temperatures. So, many efforts have been directed to develop new adsorbents, and silicas are promising materials due to their unique physical and chemical properties as well as possibility of low-cost regeneration.

MCM-41 silicas are ordered mesoporous materials with well-defined uniform pores, high surface area and pore volume. The presence of highly reactive silanol groups on silica surface opens up the possibility for introduction of various organic functional moieties into the surface layer of MCM-41. Among a large number of organic compounds appropriate for silica functionalization, cyclodextrin macromolecules are very promising

because of their capability to form inclusion complexes with chemicals of suitable geometry and functionality [23].

Here,  $\beta$ -cyclodextrin-MCM-41 silica was synthesized and tested as adsorbent for aromatic compounds removal from water. Equilibrium and kinetic multibatch adsorption experiments were carried out to elucidate benzene and phenol from aqueous solutions. The sorption properties of  $\beta$ -cyclodextrin-MCM-41 silica were compared with those of MCM-41 and aminopropyl-containing MCM-41 silicas to estimate the role of oligosaccharide groups in the process of aromatic compound removal from water.

### EXPERIMENTAL

$\beta$ -Cyclodextrin hydrate ( $\beta$ -CD) (99 %, Acros Organics), tetraethyl orthosilicate (TEOS) ( $\geq 99$  %, Merck), (3-aminopropyl)triethoxysilane (APTES) ( $\geq 99$  %, Merck), N,N'-carbonyldiimidazole (CDI) ( $\geq 98$  %, Merck), cetyltrimethylammonium bromide (CTMABr) ( $\geq 97$  %, Merck), benzene (pure analytical, Reakhim), and phenol (GR for analysis, Lachner) were used as purchased, and no further purification was performed. Aqueous ammonia 25 %, ethanol 96 %, and hydrochloric acid 37 % were purchased from Reakhim (all analytical grade) and used without additional purification. Acetone (extra pure, Merck) and N,N'-dimethylformamide (DMF) (pure analytical, Reakhim) were dried for 48 h before utilization with activated molecular sieves (0.3 nm, Merck).

**Synthesis of MCM-41-type silicas.** Hexagonally ordered MCM-41 and aminopropyl-containing MCM-41 (NH<sub>2</sub>-MCM-41) silicas were prepared by hydrothermal sol-gel synthesis in the presence of ionic surfactant compound, CTMABr, by the procedure described in [24]. TEOS or TEOS/APTES mixture was used as silica source. The final molar composition of the reaction mixture for MCM-41 and NH<sub>2</sub>-MCM-41 silicas preparing by template method was as follows: 0.1 TEOS (or 0.09 TEOS : 0.006 APTES) : 0.02 CTMABr : 0.55 NH<sub>4</sub>OH : 0.56 C<sub>2</sub>H<sub>5</sub>OH : 14.4 H<sub>2</sub>O. Obtained silicas were washed with water and dried at ambient temperature. Then, the template was removed by extraction in acid-ethanol solution.

The co-condensation method was also employed to introduce  $\beta$ -CD moieties in silica matrix. First,  $\beta$ -CD was activated with CDI to form amide bond [25]. To obtain activated oligosaccharide (**I**), a solution of CDI in dry DMF was added to a solution of anhydrous  $\beta$ -CD in dry

DMF (molar ratio CDI :  $\beta$ -CD = 1 : 1) under continuous stirring. The activation reaction was carried out at 293 K for 2 h.  $\beta$ -CD-containing organosilane (**II**) was prepared by modification of APTES with aforementioned activated oligosaccharide (**I**) at room temperature for 24 h. Then, the obtained product was used for templated sol-gel synthesis of two CD-MCM-41 silicas. One of them, CD-MCM-41-1, was prepared by co-condensation of TEOS and **II** in the presence of activation reaction products. Another silica, CD-MCM-41-2, was synthesized by use of TEOS and purified  $\beta$ -CD-organosilane. Purification of  $\beta$ -CD-organosilane was realized in accordance with the following procedure. Dry acetone was added to the reaction mixture of  $\beta$ -CD-containing organosilane (**II**) to fall out substituted oligosaccharide [26, 27], and the resultant precipitate was collected by filtration. After drying under vacuum, the yellow solid product was obtained. Finally, purified  $\beta$ -CD-organosilane was dissolved in dry DMF and co-condensed with TEOS in the presence of CTMABr. Ionic template was previously dissolved in water with stirring at room temperature, and NH<sub>4</sub>OH was added to provide the alkaline medium of the reaction. The reaction mixtures for both CD-MCM-41 silicas were agitated on magnetic stirrer for 2 h. In order to complete the condensation process, the hydrothermal treatment in autoclave at 373 K for 24 h was carried out. The final molar composition of the reaction mixture for CD-MCM-41 silicas preparing was as follows: 0.05 TEOS : 0.001  $\beta$ -CD-organosilane : 0.007 CTMABr : 0.27 NH<sub>4</sub>OH : 7.2 H<sub>2</sub>O. Both CD-MCM-41 materials were washed by small quantities of water and dried at ambient temperature. Then, the template was removed by triple solvent extraction in HCl/C<sub>2</sub>H<sub>5</sub>OH solution at room temperature for 24 h. After extraction, silicas were washed with distilled water until the negative test on halide anions with AgNO<sub>3</sub>. Obtained materials were dried in the air at 293 K.

**Characterization of MCM-41 silicas.** The ordered mesoporosity of MCM-41-type silicas was confirmed by diffraction analysis at low angles ( $2\theta=1-10$  grad) and transmission electron microscopy (TEM). Powder X-ray diffraction patterns (XRD) were measured on a DRON-4-02 diffractometer using CuK $\alpha$  radiation ( $\lambda = 0.154178$  nm) and a nickel filter. TEM experiments were carried out on a JEM JEOL 1230 electron microscope operated at 100 kV. The

transmission spectra were registered on a Thermo Nicolet NEXUS FT-IR spectrophotometer in the range from 4000 to 400  $\text{cm}^{-1}$  for solid pellets of synthesized silicas. Porosity measurements were obtained with a Kelvin-1042 Sorptometer using low-temperature adsorption-desorption of nitrogen. Prior to measurements, all samples were outgased at 413 K for 20 h. Specific surface area of MCM-41 silicas was determined using the BET method in the relative pressure range ( $P/P_0$ ) up to 0.30. The pore size distributions were calculated by applying the NLDFT (equilibrium model). The total pore volume ( $V_{\text{total}}$ ) was obtained from the amount of nitrogen adsorbed at  $P/P_0 = 0.99$ .

The amount of surface aminopropyl groups was calculated by the difference in pH values (Ionometer I-160) of starting and equilibrium acid solutions with CD-MCM-41 (or  $\text{NH}_2$ -MCM-41) silica batch after 24 h contact [28]. The content of  $\beta$ -CD in CD-MCM-41 silicas was determined by acid hydrolysis of oligosaccharide up to glucose. The concentration of glucose after the reaction with potassium ferrocyanide was defined by spectrophotometry using a Specord M-40 equipment at  $\lambda = 420 \text{ nm}$  [25, 29].

**Adsorption study.** The adsorption behavior of benzene and phenol as a function of time and equilibrium concentration was studied on MCM-41,  $\text{NH}_2$ -MCM-41, and ordered  $\beta$ -CD-containing (CD-MCM-41-1 and CD-MCM-41-2) silicas.

The kinetic and adsorption equilibrium studies were realized by the multibatch method at room temperature ( $291 \pm 1 \text{ K}$ ). For kinetic experiments, air dried weighted amounts (0.02 g) of each silica were taken in air-tight vials, then 12 ml of benzene aqueous solution ( $0.45 \text{ g}\cdot\text{L}^{-1}$ ) or 10 ml of phenol solution ( $0.64 \text{ g}\cdot\text{L}^{-1}$ ) was rapidly added. The suspensions were stirred for predetermined time intervals, then filtered through syringe filters (pores with  $d = 0.2 \mu\text{m}$ , PVDF (Millipore)) to prevent the liberation of aromatic compound. The content of benzene or phenol in filtrates was determined by UV-spectrophotometry at  $\lambda = 254$  and  $270 \text{ nm}$ , respectively.

For equilibrium adsorption experiments, aqueous solutions with benzene concentrations of  $0.036$ – $0.72 \text{ g}\cdot\text{L}^{-1}$  and phenol concentrations of  $0.06$ – $0.64 \text{ g}\cdot\text{L}^{-1}$  were used. Briefly, batches of air dried silica adsorbents (0.01 g for benzene or 0.02 g for phenol) were taken in air-tight vials, and aqueous solutions of aromatics (12 ml of benzene or 10 ml of phenol) were added. After the

absorption equilibrium was reached, the solutions were separated by syringe filter for determination of aromatic compounds concentration.

The contents of aromatics in solutions were calculated from the calibration curves prepared by plotting absorbance at 254 nm for benzene and 270 nm for phenol against certain concentrations of analytes in solutions in the range  $0.01$ – $0.45 \text{ g}\cdot\text{L}^{-1}$  or  $0.06$ – $0.64 \text{ g}\cdot\text{L}^{-1}$ , respectively.

The amount of aromatics adsorbed on MCM-41-type silicas from aqueous solutions was evaluated as:

$$a = \frac{(C_o - C_f)V}{m},$$

where  $a$  – adsorption;  $C_o$  – the initial concentration of aromatic compound in aqueous solution;  $C_f$  – the concentration of aromatics in filtrate;  $V$  – the volume of the aqueous solution of benzene (phenol);  $m$  – the mass of adsorbent.

The experimental error (%) in benzene/phenol concentration determination was calculated as follows:

$$\frac{\Delta C}{C} = \frac{\Delta A + \Delta B \cdot D + B \cdot \Delta D}{C},$$

where  $\Delta C$  – the absolute error;  $A$ ,  $B$  and  $\Delta A$ ,  $\Delta B$  – coefficients obtained from the calibration curve (an intercept and the slope) and their absolute errors at confident level 0.95, respectively;  $\Delta D$  was accepted as 0.005 (device error).

## RESULTS AND DISCUSSIONS

The synthesis of nanoporous silicas with ordered structure is an active field of research. Mesoporous MCM-41 silicas offer a number of potential advantages as adsorbents, such as high surface area, large pore volume and regular channel type pore structure. In addition, the possibility of chemical modification of MCM-41-type adsorbents by introducing specific functional groups into the silica matrix enhances their adsorption capacity. In this work, a new approach for  $\beta$ -CD-containing MCM-41 silica synthesis was demonstrated. A few mesoporous materials with ordered structure were prepared – MCM-41,  $\text{NH}_2$ -MCM-41, and two  $\beta$ -CD-MCM-41 silicas. Table 1 summarizes the structural parameters of all synthesized silicas.

To confirm that by-products of  $\beta$ -CD activation reaction could not affect the structure of the final silica, two types of CD-MCM-41 silicas

were prepared by sol-gel synthesis. The chemical nature of surface and mesoporous structure of CD-MCM-41-1 and CD-MCM-41-2 silicas obtained in the presence of  $\beta$ -CD-silane with by-products and purified one, respectively, were compared.

Characterization of CD-MCM-41-1 and CD-MCM-41-2 prepared by co-condensation method was performed using FT-IR spectroscopy, chemical analysis, XRD, TEM, and low-temperature adsorption-desorption of nitrogen.

The presence of organic component (cyclic oligosaccharide and/or aminopropyl functional groups) in MCM-41 silicas was proved by FT-IR spectroscopy and quantitative chemical analysis of silica materials. Fig. 1 shows the FT-IR spectra of the synthesized MCM-41 silicas. As can be seen from the spectrum of MCM-41 silica (Fig. 1 a, Table 1), only absorption bands attributed to the valence and deformation vibrations of silica framework (Si–O–Si and Si–OH) and remaining water molecules (H–O–H and O–H) are observed. Comparatively, in the FT-IR spectra of CD-MCM-41 silicas (Fig. 1 b, c) the absorption bands at 2986, 2946 and 1450, 1413, 1391  $\text{cm}^{-1}$  corresponding to the valence and deformation vibrations of the C–H bonds in the alkyl and glycosyl groups of incorporated compounds are

registered. Moreover, the appearance of characteristic absorption bands at 1540  $\text{cm}^{-1}$  can be attributed to the deformation vibrations of the N–H bond in the secondary amino groups of  $\beta$ -CD-silane or/and grafted functional groups. Absorption bands belonging to the deformation vibrations of the N–H bond in the residual primary amino groups (1560–1640  $\text{cm}^{-1}$ ) as well as the valence vibrations of the C=O bond in the amide linkage (near by 1700  $\text{cm}^{-1}$ ) [30] of synthesized silicas are not registered because of their overlapping with strong signal attributed to the deformation vibrations of the O–H bond in the adsorbed water molecules. Based on the results of FT-IR spectroscopy, it can be assumed the incorporation of  $\beta$ -CD-silane in the structure of silicas synthesized by templated sol-gel method. The appearance of aminopropyl groups in CD-MCM-41 points to the partial hydrolysis of amide bonds under hydrothermal treatment of  $\beta$ -CD-containing silicas in the medium of ammonium. An increase of oligosaccharide amount in CD-MCM-41-1 silica in comparison with CD-MCM-41-2 could be explained by the catalytic influence of resulting imidazole on the hydrolysis reaction of sol-gel process (Table 1).

**Table 1.** Structural parameters of synthesized MCM-41 silicas

Silica	$d_{100}$ , nm	$a$ , nm	$S_{BET}$ , $\text{m}^2\cdot\text{g}^{-1}$	$V_{total}$ , $\text{cm}^3\cdot\text{g}^{-1}$	$D_{DFT}$ , nm	Group loading				
						[–(CH <sub>2</sub> ) <sub>3</sub> NH <sub>2</sub> ],		[ $\beta$ -CD],		
						$\text{mmol}\cdot\text{g}^{-1}$	$\mu\text{mol}\cdot\text{m}^{-2}$	$\text{mmol}\cdot\text{g}^{-1}$	$\mu\text{mol}\cdot\text{m}^{-2}$	
MCM-41	4.17	4.82	995	0.75	3.7	5.1	–	–	–	–
NH <sub>2</sub> -MCM-41	4.02	4.64	523	0.86	3.7	5.1	0.44	0.84	–	–
CD-MCM-41-1	4.11	4.75	812	1.06	3.9	5.1	0.05	0.06	0.018	0.022
CD-MCM-41-2	4.11	4.75	802	1.38	3.9	5.2	0.04	0.05	0.010	0.012

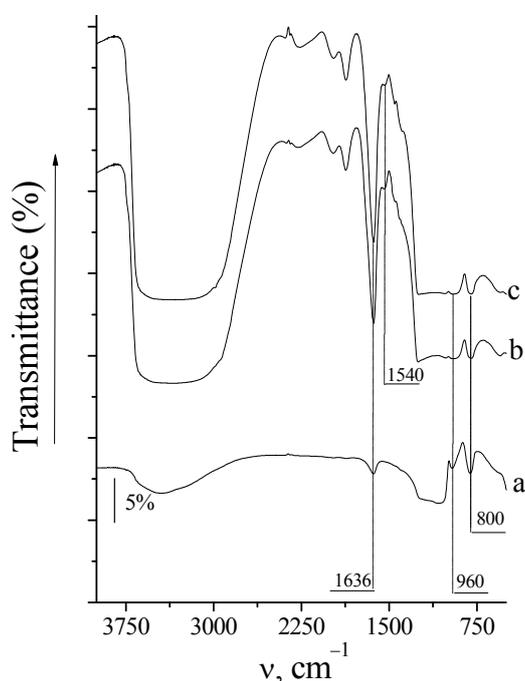
Hexagonally ordered pore structure of obtained silicas was confirmed by XRD and TEM analyses. As could be clearly seen from the Fig. 2, the unidimensional cylindrical pores of CD-MCM-41 silicas are arranged in a honeycomb structure. Also, XRD patterns of synthesized CD-MCM-41 silicas are shown in Fig. 2 (inset). The presence of diffraction peaks at  $2\theta = 2.15$  are attributed to the (100) reticular planes in CD-MCM-41-1 and CD-MCM-41-2 silicas. Moreover, distinct reflexes on the XRD patterns between 3.5 and 5 grad could be indexed to the (110) and (200) reticular planes of hexagonally packed pores and confirm the

formation of two-dimensionally periodic hexagonal lattice, which is characteristic for MCM-41 materials. Structural parameters (interplanar distance  $d$  and unit cell parameter  $a$ ) calculated from XRD analysis for all silicas are summarized in Table 1. Besides, the same values of  $d$  and  $a$  diffraction parameters of CD-containing silicas denote that the presence of activation reaction products in CD-MCM-41-1 sol-gel synthesis has no noticeable effect on forming of ordered hexagonal network of pores.

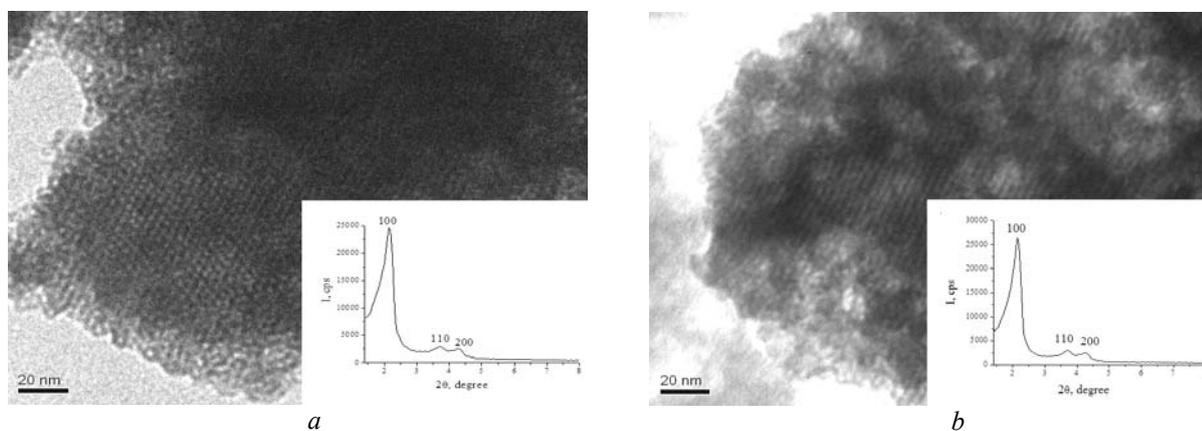
Fig. 3 displays isotherms of nitrogen adsorption-desorption and pore size distributions

for CD-MCM-41-1 and CD-MCM-41-2 silicas. Nitrogen adsorption at low relative pressures  $P/P_0 < 0.3$  for CD-MCM-41 silicas is attributed to the monolayer adsorption, following multilayer adsorption on the walls of mesopores. The distinct step on the isotherm at  $P/P_0 \sim 0.35$  indicates a uniformly porous surface. The pore size distribution plots clearly demonstrate that uniform pores are prevailing in CD-MCM-41 materials causing the high peak centered at 3.9 nm. The appearance of larger pores (slight peak above 5 nm) can be explained by partial degradation of the walls between individual channels of pores in the process of hydrothermal treatment carried out at 373 K in the medium of ammonia. Also, the

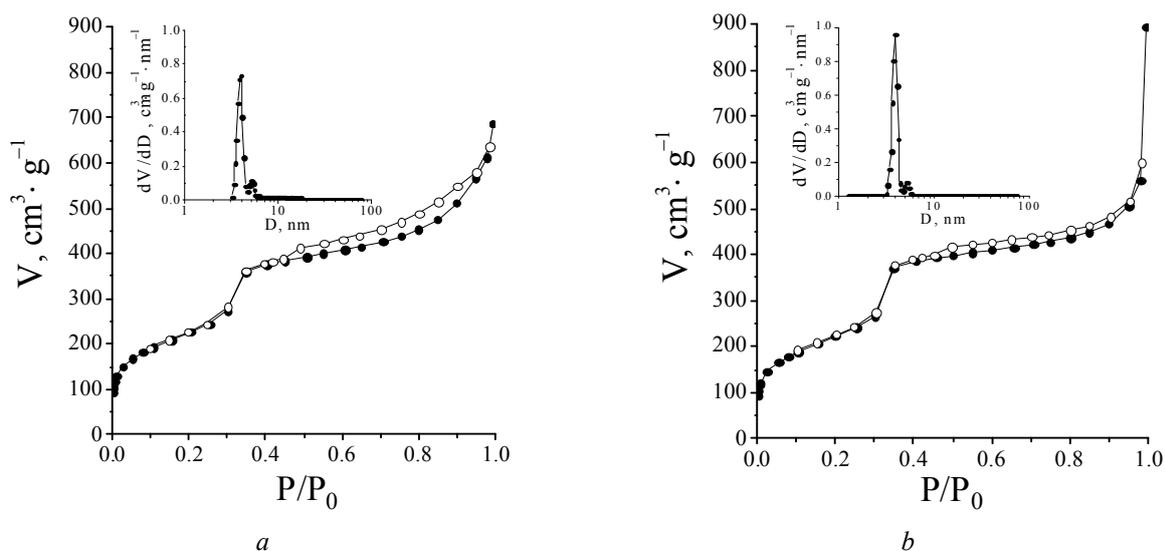
CD-MCM-41-1 and CD-MCM-41-2 isotherms similarity confirms that by-products of  $\beta$ -CD activation reaction do not affect the pore structure of the resulting silica. The values of BET specific surface area for CD-MCM-41 silicas calculated from linear region of isotherms are more than  $800 \text{ m}^2 \cdot \text{g}^{-1}$ . Early, it was demonstrated the incorporation of cyclodextrin into mesostructured silica by templated synthesis with 1,3,5-trimethylbenzene as a pore-expanding agent [31]. It is worth noting that here  $\beta$ -CD-containing silicas with high surface areas, pore volume, and large-scale ordering were managed to get by sol-gel method without any pore-expanding agent.



**Fig. 1.** IR spectra of MCM-41 (a), CD-MCM-41-1 (b), and CD-MCM-41-2 (c) silicas



**Fig. 2.** TEM images and XRD patterns (inset) of CD-MCM-41-1(a) and CD-MCM-41-2 (b) silicas

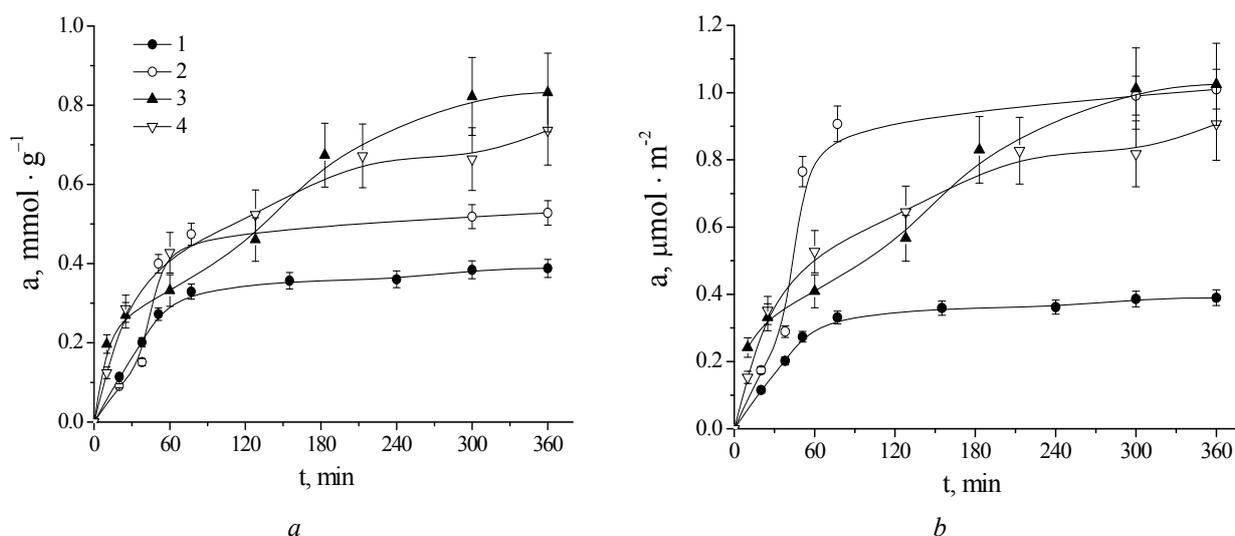


**Fig. 3.** Nitrogen adsorption-desorption isotherms and NLDFT pore diameter of CD-MCM-41-1 (a) and CD-MCM-41-2 (b). Solid symbols denote adsorption, and open ones denote desorption

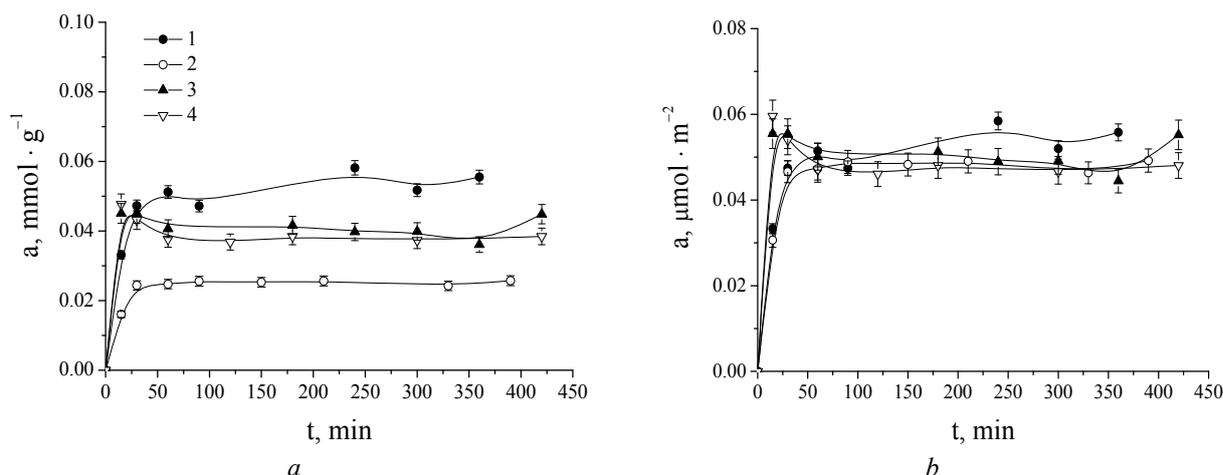
Incorporation of cyclic oligosaccharide into solid supports like MCM-41 silicas makes possible an efficient removing of aromatic pollutants from aqueous solutions by means of supramolecular structures formation. Here, adsorption behavior of functionalized MCM-41 silicas was studied by removing of benzene and phenol from aqueous solutions.

Adsorption kinetic experiments were carried out to evaluate a period which should be sufficient to reach adsorption equilibrium. Fig. 4 represents the kinetic curves for benzene uptake from aqueous solutions with MCM-41,

$\text{NH}_2$ -MCM-41, CD-MCM-41-1, and CD-MCM-41-2 silicas. The adsorption of benzene on MCM-41 and  $\text{NH}_2$ -MCM-41 silicas is characterized by rapid uptake of aromatic molecules within the first hour until it slows down and becomes constant at 5 h. For CD-MCM-41 silicas, adsorptive uptake of benzene increases slowly and becomes constant in about 6 h. The adsorption kinetic curves of phenol on CD-MCM-41 silicas followed an ascending trend with time in the region up to one hour (Fig. 5).



**Fig. 4.** Kinetic curves of benzene adsorption on MCM-41 (1),  $\text{NH}_2$ -MCM-41 (2), CD-MCM-41-1 (3), and CD-MCM-41-2 (4) silicas per g (a) or per  $\text{m}^2$  (b) of materials



**Fig. 5.** Kinetic curves of phenol adsorption on MCM-41 (1), NH<sub>2</sub>-MCM-41 (2), CD-MCM-41-1 (3), and CD-MCM-41-2 (4) silicas per g (a) or per m<sup>2</sup> (b) of materials

It was shown that  $\beta$ -CD and aromatic compounds could form “host – guest” inclusion complexes in aqueous solutions. The formation of “ $\beta$ -CD – aromatic compound” complexes is spontaneous and thermodynamically profitable exothermal process [32, 33]. The equilibrium adsorption study was used to evaluate the role of cyclic oligosaccharide fragments as specific adsorption sites of ordered CD-MCM-41 silicas. The adsorption isotherms of benzene from aqueous solutions as quantity of benzene adsorbed per unit weight of silica or per unit of adsorbent surface are given in Fig. 6 a and 6 b, respectively. The adsorption of benzene on silicas based on interactions of the aromatic ring of  $\pi$ -electrons with the surface silanol groups is well known [34]. It can be seen that adsorption isotherms of benzene on MCM-41 and NH<sub>2</sub>-MCM-41 silicas have concave shape in the region of small equilibrium concentrations of adsorbate as a result of weak affinity of non-polar aromatic rings to polar silanol groups, but then followed a sharp increase of aromatic uptake. Obviously, it could be explained by the reorientation of benzene molecules owing to increase in its concentration in the solutions. As follows, the more benzene is already adsorbed, the easier it is for additional amounts to become fixed as a result of hydrophobic interaction [35]. The character of benzene adsorption on the surface of CD-MCM-41 silicas is considerably different. In the region of small equilibrium concentrations, the higher adsorption of benzene compared to MCM-41 and NH<sub>2</sub>-MCM-41 silicas is observed. Apparently, the uptake of benzene molecules is caused by non-specific binding interaction with

silica matrix as well as selective binding sites within its structure.

It has been shown that typical adsorption capacities for carbon and silica adsorbents in liquid phase under different conditions are in the range of 12–230 mg · g<sup>-1</sup> for benzene [36, 37]. Therefore, prepared CD-MCM-41 silicas demonstrate adsorption level performance of known samples (up to 87 mg · g<sup>-1</sup> in studied concentration diapason), and could be very promising for the treatment of aqueous solutions with low benzene concentration.

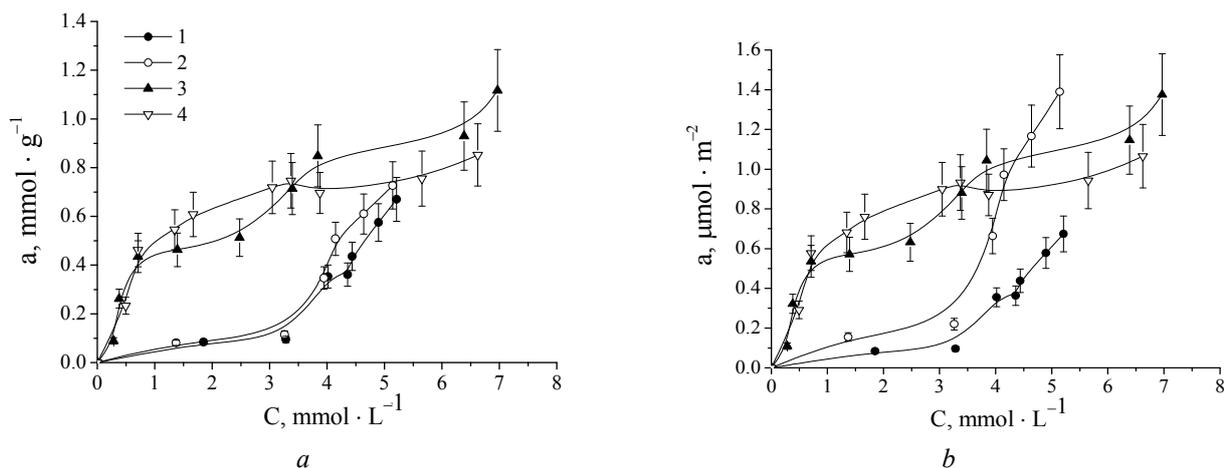
The adsorption equilibrium data of synthesized silicas for phenol are shown in Fig. 7. It can be seen that phenol adsorption performance is weak in comparison with benzene one, which is consistent with the literature [36, 37]. Despite low adsorbed amount of phenol, different adsorption behavior of MCM-41, NH<sub>2</sub>-MCM-41 and CD-MCM-41 silicas are clearly seen (Fig. 7).

The significant uptake of phenol on CD-MCM-41 silicas in comparison with MCM-41 and NH<sub>2</sub>-MCM-41 is observed at equilibrium concentration around 3 mmol · L<sup>-1</sup>. Here, the amount of phenol removed from aqueous media is almost equal to  $\beta$ -CD content into CD-MCM-41-1 and CD-MCM-41-2 silicas, confirming the chemical incorporation of  $\beta$ -cyclodextrin and its availability for specific hydrophobic interactions with phenol molecules (1 : 1 inclusion complex formation). In general, adsorption of phenol on CD-MCM-41 silica involves hydrophobic interactions of phenol molecules with surface  $\beta$ -CD moieties as well as interactions of the aromatic ring of  $\pi$ -electrons with the surface silanol groups and

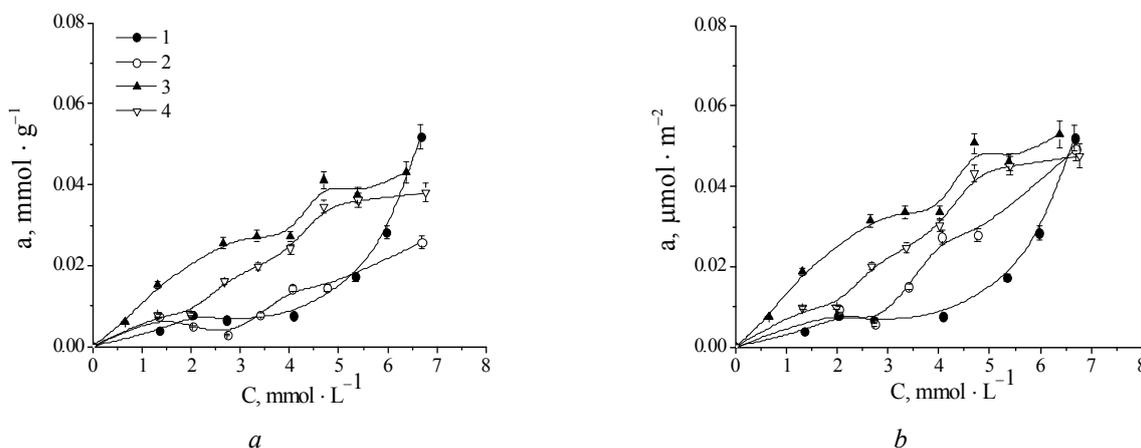
acid-base interactions of phenol hydroxyl groups with surface amine groups.

A close inspection of benzene/phenol adsorption isotherms on MCM-41, NH<sub>2</sub>-MCM-41, CD-MCM-41-1, and CD-MCM-41-2 silicas reveals that the uptake of aromatic molecules from aqueous solutions is efficient for materials with incorporated oligosaccharide molecules in the equilibrium concentration up to 4–5 mmol · L<sup>-1</sup>. In comparison, at comparatively high concentrations

adsorption effectiveness of all studied silicas is almost the same. This signifies that synthesized β-CD-MCM-41 silica can act as effective adsorbents for trace amounts of aromatic compounds in water systems. Moreover, the higher adsorption performance of β-CD-MCM-41 silicas towards benzene and their adsorptive affinity to phenol can be useful in the separation of aromatic compounds.



**Fig. 6.** Benzene adsorption isotherms on MCM-41 (1), NH<sub>2</sub>-MCM-41 (2), CD-MCM-41-1 (3), and CD-MCM-41-2 (4) silicas per g (a) or per m<sup>2</sup> (b) of materials



**Fig. 7.** Phenol adsorption isotherms on MCM-41 (1), NH<sub>2</sub>-MCM-41 (2), CD-MCM-41-1 (3), and CD-MCM-41-2 (4) silicas per g (a) or per m<sup>2</sup> (b) of materials

## CONCLUSIONS

In this study, we report on the synthesis and characterization of β-cyclodextrin-MCM-41 silica obtained with β-cyclodextrin-containing silane in the presence of ionic template (cetyltrimethyl-

ammonium bromide). β-Cyclodextrin-silane was prepared by modification of (3-aminopropyl)triethoxysilane with oligosaccharide activated by N,N'-carbonyldiimidazole. On the basis of XRD, TEM, low-temperature adsorption-desorption of nitrogen, FT-IR spectroscopy and quantitative

chemical analysis, it has been shown that obtained silica is a well-ordered mesoporous material with high surface area (about  $800 \text{ m}^2 \cdot \text{g}^{-1}$ ) and sufficient oligosaccharide group loading (up to  $0.022 \mu\text{mol} \cdot \text{m}^{-2}$ ). Also, the adsorption of aromatic compounds (benzene and phenol) from aqueous solutions on the surface of  $\beta$ -cyclodextrin-MCM-41 silica was studied as a

function of time and equilibrium concentration. The improved adsorption properties of synthesized material were observed and compared with MCM-41 and  $\text{NH}_2$ -MCM-41 silicas. The proposed synthesis approach may be applicable for obtaining of ordered  $\beta$ -CD-containing functional materials with high affinity to aromatic compounds of suitable geometry for water purification.

## **$\beta$ -Циклодекстрин-MCM-41 кремнезем як перспективний адсорбент для вилучення слідових кількостей ароматичних сполук з води**

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*У цьому дослідженні здійснено золь-гель синтез  $\beta$ -циклодекстрин-MCM-41 кремнезему з використанням  $\beta$ -циклодекстринвмісного силану і тетраетилортосилікату (як джерел кремнезему) в присутності йонного темплату (цетилтриметиламоній броміду).  $\beta$ -Циклодекстринвмісний силан було одержано шляхом модифікування (3-амінопропіл)триетоксисилану олігосахаридом, який активували у присутності  $N,N'$ -карбонілдіімідазолу. Успішне введення  $\beta$ -циклодекстринових фрагментів у кремнезем було підтверджено за допомогою Фур'є-ІЧ спектроскопії та кількісного хімічного аналізу. Одержаний  $\beta$ -циклодекстрин-MCM-41 кремнезем охарактеризовано методами рентгенівської дифракції, трансмісійної електронної мікроскопії та низькотемпературної адсорбції-десорбції азоту. Вивчено адсорбцію бензену та фенолу з водних розчинів на  $\beta$ -циклодекстрин-MCM-41 кремнеземі в залежності від тривалості контакту та рівноважної концентрації адсорбтиву. Продемонстрована більша специфічність адсорбції ароматичних сполук на  $\beta$ -циклодекстрин-MCM-41 кремнеземі у порівнянні з MCM-41.*

**Ключові слова:** MCM-41,  $\beta$ -циклодекстрин, золь-гель синтез, адсорбція, ароматичні сполуки

## **$\beta$ -Циклодекстрин-MCM-41 кремнезем как перспективный адсорбент для извлечения следовых количеств ароматических соединений из воды**

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*В этом исследовании осуществлен золь-гель синтез  $\beta$ -циклодекстрин-MCM-41 кремнезема с использованием  $\beta$ -циклодекстринсодержащего силана и тетраэтилортосиликата (в качестве источников кремнезема) в присутствии ионного темплата (цетилтриметиламмоний бромид).  $\beta$ -циклодекстринсодержащий силан был получен путем модифицирования (3-аминопропил)триетоксисилана олигосахаридом, активированным  $N,N'$ -карбонилдиимидазолом. Успешное введение  $\beta$ -циклодекстриновых фрагментов в кремнезем было подтверждено с помощью Фурье-ИК спектроскопии и количественного химического анализа. Полученный  $\beta$ -циклодекстрин-MCM-41 кремнезем охарактеризован методами рентгеновской дифракции, трансмиссионной электронной микроскопии и низкотемпературной адсорбции-десорбции азота. Изучена адсорбция бензола и фенола из водных растворов на  $\beta$ -циклодекстрин-MCM-41 кремнеземе в зависимости от длительности контакта и равновесной концентрации адсорбтива. Продемонстрирована более высокая специфичность адсорбции ароматических соединений на  $\beta$ -циклодекстрин-MCM-41 кремнеземе по сравнению с MCM-41.*

**Ключевые слова:** MCM-41,  $\beta$ -циклодекстрин, золь-гель синтез, адсорбция, ароматические соединения

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