

## Adsorption properties of silica with covalently bound 8-hydroxyquinoline with respect to toxic metal ions

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Conditions of a single-stage chemical binding of 8-hydroxyquinoline molecules to the surface of inorganic matrix using of the Mannich aminomethylation reaction and adsorption properties of so obtained chemically modified silica with respect to ions of toxic metals have been studied. The synthetic method provides a high concentration and a homogeneous distribution of complexing groups over the surface, and the adsorbent obtained displays a high capacity to some environmentally toxic metals (>2 mmol/g) and satisfactory adsorption kinetic properties, thus making it possible to use the adsorbent for the ion preconcentration both in static and dynamic modes. The structure studies of toxic metal complexes with 8-hydroxyquinoline immobilized at silica surface by ESR and IR spectroscopy testify that the metal ions are co-ordinated with bound ligand through nitrogen and oxygen atoms.

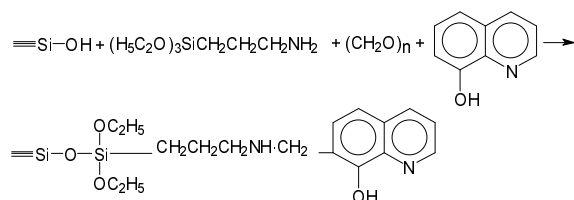
Исследованы условия одностадийного метода химического закрепления молекул 8-оксихинолина путем осуществления в поверхностном слое неорганической матрицы реакции аминометилирования Манниха и адсорбционные свойства полученного химически модифицированного кремнезёма по отношению к ионам токсичных металлов. Метод синтеза обеспечивает равномерное распределение и высокую концентрацию комплексообразующих групп на поверхности, а полученный сорбент имеет высокую сорбционную емкость по отношению к большинству токсичных металлов (>2 ммоль/г) и хорошие кинетические характеристики, что позволяет использовать адсорбент для предконцентрирования ионов как в статическом, так и в динамическом режиме. Исследования строения комплексов токсичных металлов с иммобилизованным на поверхности кремнезема 8-оксихинолином методами ЭПР и ИК-спектроскопии свидетельствуют о координации ионов металлов с закрепленным лигандом через атомы азота и кислорода.

8-Hydroxyquinoline (oxine) forms molecular complexes with almost all transition metals, but the complex formation reactions run best with ions of toxic elements such as aluminium(III), zinc(II), lead(II), copper(II), bismuth(III), tin(IV), chromium(III, VI), arsenic(V), molybdenum(V, IV), and others. The oxine molecules bound to the carrier (polymers, silicas, metal oxides) surfaces retain their complexing ability with respect to metal ions. Such immobilized reagents are

used successfully for concentration and separation of metal ions from aqueous solutions [1–6]. The oxine-containing polymer resins are characterized by a significant sorption capacity and a high efficiency of water purification. However, such polymer adsorbents also have drawbacks such as a high swelling and low sorption rate. In contrast, silica matrices with immobilized 8-hydroxyquinoline exhibit good kinetic properties but a lower sorption capacity. During

the immobilization procedure, it is of importance to retain the properties of the reagent complexing groups. That is why beginning from the first work by Hill [7], the 8-hydroxyquinoline was bound to the surface using the azo-coupling reaction (introducing amino-containing aromatic compounds, diazotization, and azo-coupling). That multi-stage process results in a heterogeneous modifying layer and low concentrations of bound oxine molecules. Attempts were made to improve the situation using oxine derivatives containing additional functional groups to bind the reagent to the surface of untreated or modified carrier [8–10]. Of greatest interest, however, is the use of Mannich reaction to immobilize 8-hydroxyquinoline and other phenolic type analytical reagents [11–15]. As is shown in our previous study [15], the single-stage aminomethylation reaction can be used to bind oxine molecules to a silica surface. The main purpose of this work is to study the adsorption properties of such silicas with covalently bound 8-hydroxyquinoline with respect to toxic metal ions.

8-Hydroxyquinoline molecules were bound to the silica surface using the method developed before [15] that comprises the use of amino-containing alkoxy-silane and paraformaldehyde according to the following scheme:



Silica gel with a specific surface area of 256 m<sup>2</sup>/g (Merck, particle size 0.06–0.16 mm) was used as a carrier. A weighted sample of 8-hydroxyquinoline (730 mg, 5 mmol) was dissolved in 5–10 ml of ethyl alcohol under a mild heating. Then the volume was increased to 15 ml and 0.3 g (10 mmol) of paraformaldehyde, 1 ml (5 mmol) 3-aminopropyltriethoxysilane, and 10 g of pure silica gel were added. The mixture was heated at 60°C for 5 h under periodic stirring. The modified silica was dried at 100°C for 2 h, then washed with ethanol (7×20 ml) and dried again at 120°C for 1.5 h.

To verify the binding of 8-hydroxyquinoline molecules to the silica surface, IR-spectrum of the modified silica has been recorded (Fourier transform IR spectrometer

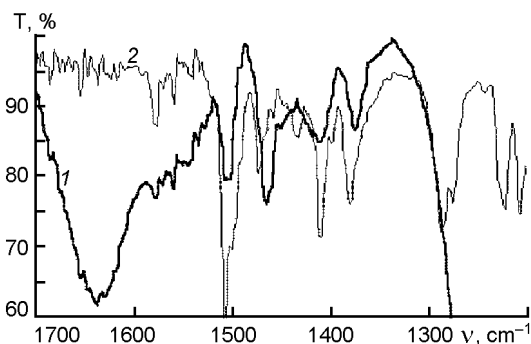


Fig. 1. FTIR-spectra of 8-hydroxyquinoline (2) and silica gel with covalently bound oxine (1).

Nexus 470). The degree of ions adsorption on surface of the silica with chemically bound 8-Hydroxyquinoline was calculated by the following formula:  $R = m_{\text{ads}}/m_0 \cdot 100\%$ , where  $m_{\text{ads}}$  is a weight of adsorbed metal and  $m_0$  is a metal contents in the initial solution. The value of  $m_{\text{ads}}$  was determined by subtracting the metal concentration in an equilibrium solution after adsorption from the  $m_0$  magnitude.

When studying the metal ion adsorption, Pb(II), Zn(II), Cd(II), Fe(III), Al(III), Cu(II) and Mo(VI) solutions were studied photometrically using a SF-46 spectrophotometer with a quartz square cuvette  $l = 1$  cm at the following wavelengths: for copper(II),  $\lambda = 490$  nm, for aluminium(III),  $\lambda = 640$  nm, for zinc(II),  $\lambda = 455$  nm, for cadmium(II),  $\lambda = 500$  nm, for lead(II),  $\lambda = 520$  nm, for iron(III),  $\lambda = 510$  nm, and for molybdenum(VI),  $\lambda = 470$  nm. The equilibrium concentrations of metal ions were determined by spectrophotometry according to [16]. The electron spin resonance spectra of copper(II) complexes with bound 8-hydroxyquinoline molecules were measured using a RE-3106 radiospectrometer (Russia) operated in the 3 cm wavelength range.

The intense absorption bands of silica matrix are observed in the wavelength region less than 1250 cm<sup>-1</sup> (Fig. 1). This fact hinders the analysis of the modified sample IR-spectrum. At the same time, the 1250–1600 cm<sup>-1</sup> region is informative enough to make a conclusion about chemical binding of 8-hydroxyquinoline molecules to the silica surface. Comparing IR-spectra of the synthesized adsorbent (curve 1) and of 8-hydroxyquinoline (curve 2), the presence of absorption band at 1580 cm<sup>-1</sup> (stretching vibrations of C–N bonds) was noted in both cases. There are also bands at 1510 cm<sup>-1</sup>

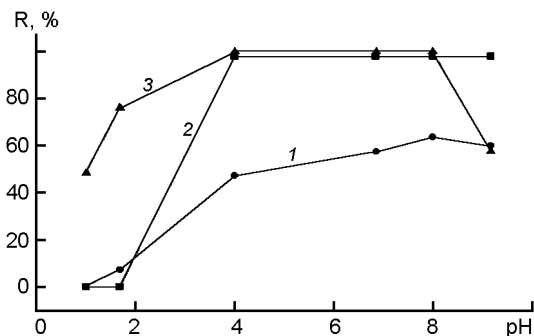


Fig. 2. Dependence of  $\text{Cd}^{2+}$  (1),  $\text{Zn}^{2+}$  (2) and  $\text{Pb}^{2+}$  (3) ion adsorption level by silica with immobilized 8-hydroxyquinoline on the solution pH.

(the most intense band) and at 1470, 1440, 1410 and 1380  $\text{cm}^{-1}$ , which correspond to skeletal vibrations of aromatic C–C bonds and C–O–H groups. The presence of these intense bands after long-term washing of the sample in ethanol testifies the chemical binding of 8-hydroxyquinoline molecules to the silica surface.

The adsorption properties of the obtained silica with immobilized 8-hydroxyquinoline were studied initially in the static mode. To that end, 0.1 g of the adsorbent per 25 ml of metal solution was used. For these experiments, we have selected ions of some metals belonging to the 1st toxicity group, namely, lead(II), cadmium(II), zinc(II), and to the 2nd toxicity group, namely, aluminium(III), copper(II), iron(III) and molybdenum(VI), which form stable complexes with 8-hydroxyquinoline in solutions.

Table 1 presents the data demonstrating the metal ion adsorption level of the modified adsorbent depending on the medium pH. According to these results, the synthesized silica with immobilized 8-hydroxyquinoline can be inferred to extract quantita-

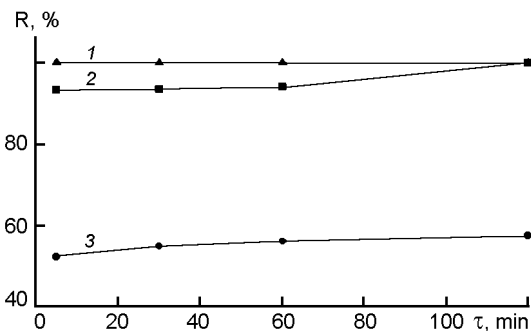


Fig. 3. Dependence of extraction degree of  $\text{Pb}^{2+}$  (1),  $\text{Zn}^{2+}$  (2) and  $\text{Cd}^{2+}$  (3) ions by silica with covalently bound 8-hydroxyquinoline on adsorption time at pH = 6.86.

tively  $\text{Pb(II)}$ ,  $\text{Fe(III)}$ ,  $\text{Zn(II)}$  ions, to adsorb almost completely (90–98 %)  $\text{Cu(II)}$ ,  $\text{Mo(VI)}$  ions and to separate only partially (60–80 %)  $\text{Cd(II)}$  and  $\text{Al(III)}$  ions out of neutral and slightly basic solutions (at pH = 6–9). In the acidic region (at pH = 1–4), the adsorbent extracts quantitatively zinc(II), lead(II), iron(III) ions, adsorbs almost completely (96–99 %) copper(II), aluminium(III) and molybdenum(VI) ions and separates partially cadmium(II) ions (Fig. 2).

Data presented in Table 2 characterize the adsorption rate of the toxic metal ions by the synthesized adsorbent. Among metals of the 1st toxicity group, the modified silica adsorbent displays the best kinetic characteristics with respect to lead(II) ions which were fully extracted for 5 min. Full adsorption of zinc(II) ions takes place only for 2 h. The degree of  $\text{Cd(II)}$  ions adsorption does not exceed 59 % even after contact with the adsorbent for 24 h (Fig. 3). Among metals of the 2nd toxicity group, silica gel with immobilized oxine exhibits the best kinetic characteristics with respect to iron(III) and copper(II) ions. Maximum

Table 1. Dependence of adsorption level (%) of some metals of I and II toxicity group by silica gel with covalently bound 8-hydroxyquinoline on the solution pH (static adsorption mode, weighted sample 0.1 g, metal content in the solution 100  $\mu\text{g}$ , adsorption time 2 h).

Metal ion	pH = 1.0	pH = 1.7	pH = 4.0	pH = 5.7	pH = 6.8	pH = 8.0	pH = 9.2
$\text{Zn}^{2+}$	0	0	100	71.2	100	100	100
$\text{Cd}^{2+}$	0	7.5	47.5	32.5	67.5	63.8	60.0
$\text{Pb}^{2+}$	48.4	76.1	100	100	100	100	57.5
$\text{Cu}^{2+}$	97.0	99.3	97.6	98.4	99.3	94.0	98.1
$\text{Fe}^{3+}$	6.7	100	74.0	14.4	100	89.5	100
$\text{Al}^{3+}$	0	95.6	70.6	63.0	89.8	74.8	95.6
$\text{Mo}^{6+}$	84.9	97.2	95.8	97.2	96.2	97.2	40.4

extraction of molybdenum(VI) and aluminium (III) ions does not exceed 97 % even after prolonged contact time with the adsorbent surface. On the whole, these results support the conclusion that silica with covalently bound 8-hydroxyquinoline synthesized by the single-stage Mannich aminomethylation reaction is characterized by a satisfactory adsorption rate of toxic metal ions and can be used to extract thereof out of aqueous solutions both in the static and dynamic modes.

To determine the maximum sorption capacity, experiments were carried out with solutions containing a large amount of metal ions (1–5 mmol per 1 g of adsorbent). The results obtained testify that silica gel with immobilized 8-hydroxyquinoline synthesized by the single-stage Mannich reaction possesses significantly higher sorption capacity with respect to toxic metal ions (>2 mmol/g) as compared to that for the chemically modified silicas prepared by appropriate multi-stage procedure [5]. Thus, the proposed synthesis method of allows one to obtain silica with sufficiently high concentration of complexing groups in the surface layer that permits to use such adsorbents for preconcentration of toxic metals ions and for the effective purification of water.

According to ESR and IR-spectroscopy, adsorption of toxic metals on the chemically modified silica gel occurs under formation of complexes between metal ions and 8-hydroxyquinoline chemically bound to the silica surface. In particular, in the IR-spectra of zinc(II), aluminium(III), copper(II) and molybdenum(VI) complexes with bound 8-hydroxyquinoline, a shift of the absorption band at  $3420\text{ cm}^{-1}$  (in the spectrum of modified silica) to  $3410\text{ cm}^{-1}$  (for adsorption complexes with metal ions) is observed.

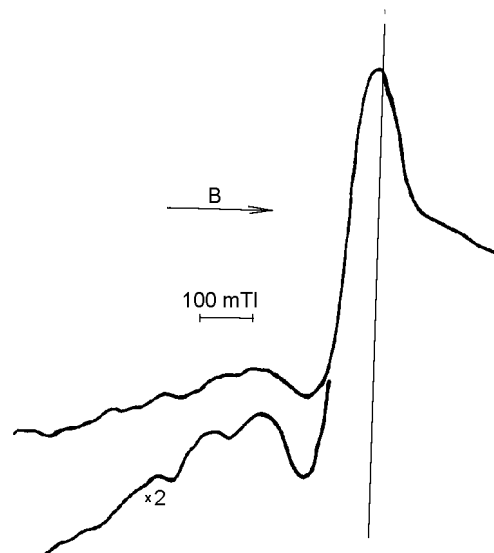


Fig. 4. ESR spectra of complexes of copper(II) ions with 8-hydroxyquinoline covalently bound with the silica surface.

These results testify to involvement of NH-groups of bound 8-hydroxyquinoline in formation of the adsorption complexes. The frequency shift (by about  $10\text{ cm}^{-1}$ ) of absorption bands at  $1580$  and  $1540\text{ cm}^{-1}$  in the spectra of complexes may testify to additional coordination of metal ions through the hydroxylic oxygen atom of the immobilized 8-hydroxyquinoline molecules.

The data on structure of copper(II) complexes with bound 8-hydroxyquinoline were obtained from ESR spectra (Fig. 4). According to calculations based on these spectra, the principal values of the  $g_{\parallel}$ -factor is  $2.372$ , and  $g_{\perp} = 2.064$ , the hyperfine coupling constant  $A = 201 \cdot 10^{-4}\text{ cm}^{-1}$ . This allows one to assume the nearest coordination surrounding of  $\text{Cu}^{2+}$  ions in the surface complex. Most probably,  $4[\text{O}]$  and  $2[\text{N}]$  dis-

Table 2. Adsorption kinetics (%) of some metal ions of the 1st and the 2nd toxicity groups by silica with covalently bound 8-hydroxyquinoline (static adsorption mode, weighted sample 0.1 g, metal content in the solution  $100\text{ }\mu\text{g}$ , pH = 6.8)

Metal ion	Adsorption time				
	5 min.	30 min.	60 min.	120 min.	24 h
Zn <sup>2+</sup>	93.2	93.5	94.0	100	100
Cd <sup>2+</sup>	52.5	55.0	56.2	57.5	58.8
Pb <sup>2+</sup>	100	100	100	100	100
Cu <sup>2+</sup>	94.0	99.3	99.3	99.3	100
Fe <sup>3+</sup>	100	100	100	100	100
Al <sup>3+</sup>	93.9	93.9	94.2	96.8	
Mo <sup>6+</sup>	95.8	92.4	91.0	91.5	96.7

torted octahedron structures are formed with O atoms of hydroxyl groups in the equatorial position and N atoms in the axial position, or with N atom and two O atoms in the equatorial position and two O atoms in the axial position [17, 18].

To conclude, silica gel with covalently bound 8-hydroxyquinoline obtained by the single-stage Mannich reaction quantitatively extracts ions of toxic metals such as lead (II), zinc(II), aluminium(III), copper(II), iron(III), and molybdenum(VI) in the static adsorption mode at pH from 4 to 8. Cadmium(II) ions are adsorbed in these conditions only partially. The modified adsorbent is characterized by satisfactory kinetics of metal extraction and can be used for their separation in the dynamic adsorption mode. Unlike analogous chemically modified silicas obtained in multi-stage process, the synthesized adsorbent has a significantly higher sorption capacity with respect to toxic metal ions and can be used to purify water effectively. As it follows from ESR and IR spectroscopy data, the metals are adsorbed on the modified silica surface due to complexing between metal ions and 8-hydroxyquinoline chemically bound on the silica surface. Study of the structure of the surface complexes testifies coordination of metals through nitrogen atoms as well as under involvement of hydroxylic oxygen atoms of the immobilized 8-hydroxyquinoline molecules.

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## Адсорбційні властивості кремнеземів з ковалентно закріпленим 8-оксихіноліном щодо іонів токсичних металів

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Досліджено умови одностадійного методу хімічного закріплення молекул 8-оксихіноліну шляхом здійснення у поверхневому шарі неорганічної матриці реакції амінометилування Манніха та адсорбційні властивості одержаного хімічно модифікованого кремнезему щодо іонів токсичних металів. Метод синтезу забезпечує рівномірний розподіл та високу концентрацію комплексуютьючих груп на поверхні, а одержаний сорбент виявляє високу сорбційну ємність відносно до більшості токсичних металів (>2 ммоль/г) та хороші кінетичні характеристики, що дозволяє використовувати адсорбент для передконцентрування іонів як у статичному, так і у динамічному режимі. Дослідження будови комплексів токсичних металів з імобілізованим на поверхні кремнезему 8-оксихіноліном методами ЕПР та ІЧ-спектроскопії свідчать про координацію іонів металів із закріпленим лігандом через атоми нітрогену і кисню.