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ION-EXCHANGE PROPERTIES OF MODIFIED SILICA WITH BOUND AMIDES OF POLYHEXAMETHYLENEGUANIDINE AND MALEIC OR *O*-PHTHALIC ACIDS

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Amides of polyhexamethyleneguanidine and maleic or o-phthalic acids were chemically bound with the silica surface. Adsorption properties of synthesized modified silicas have been studied with respect to V(V)-, Cr(VI)-, Mo(VI)-, and W(VI)-containing anions. Both of adsorbents were found to show high adsorption activity in the acidic and slightly acidic media. Kinetic parameters of the obtained composites are closely similar to a polymeric adsorbent. Reduction of Mo(VI) and Cr(VI) ions was detected at adsorption on silica with bound amide of polyhexamethyleneguanidine and o-phthalic acid. The investigation demonstrates the possibility of the quantitative determination of microamounts of the studied metals in the adsorbent phase using the X-ray-fluorescence analysis after extraction of anions from a solution.

INTRODUCTION

Chemically modified silicas with immobilized organic ligands are widely used for solid-phase extraction, separation and concentration of metal-containing anions and cations of transition metals because of their complexing and ion-exchanging properties [1–7]. Many of the drawbacks of organic ion-exchangers, such as significant solvent swelling effects, slower sorption kinetics, lower thermal, radiation and microbial stability can be removed by means of application of such inorganic adsorbents. But usually modified silica carriers have a low adsorption capacity and many efforts have been made to improve this important property, thus opening the possibility for wider applications. In particular, silica adsorbents with immobilized functional polymers can combine the advantages of the inorganic matrix with the sufficiently high sorption capacity of organic polymers.

Multifunctional polymers containing quaternary nitrogen atoms are very promising for the silica adsorbents modification [8–14]. Polyhexamethyleneguanidine hydrochloride (PHMG) belongs to the type of polymers which manifests

properties of polyamines and quaternary ammonium compounds (availability of guanidine group containing two substituted and one protonated amino groups) [15]. PHMG displays well-expressed complexing properties with respect to metal ions [16–18]. PHMG is a water-soluble anion-exchange resin with a moderate basicity and biocide properties and this polymer can be applied for the simultaneous water decontamination and purification from toxic anions and cations. Inorganic sorbents containing immobilized polyhexamethyleneguanidine were successfully used for preconcentration and removal metal ions from water solutions [13, 14, 19–28]. Chemical modification of PHMG by means of introducing additional nitrogen-, sulfur- or oxygen-containing ligands can offer new possibilities to obtain polymers and adsorbents with a higher potential of complexing and ion-exchanging properties. It was reported in our previous paper [29] that immobilized amides of polyhexamethyleneguanidine with maleic (PHMG-MA) and *o*-phthalic (PHMG-PA) acids have fairly good complexing properties with respect to the cations of transition metals. A silica chemically modified with these polymers can quantitatively remove cations of

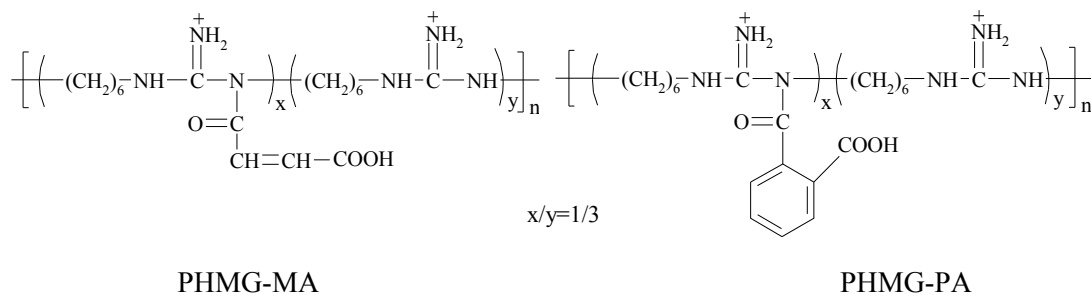
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Zn(II), Cu(II) and Fe(III) from aqueous solutions. Metal ions separation occurs in the weakly alkaline media. Under these conditions, the polymers under study exist in deprotonated form and behave similarly to typical amine compounds.

The aim of this work was to study the ion-exchanging properties of silicas with covalently bound PHMG-MA or PHMG-PA with respect to V(V)-, Cr(VI)-, Mo(VI)-, and W(VI)-containing anions.

MATERIALS AND METHODS

Reagents. Starting solutions with a concentration of 1 mg/ml were prepared by way of dissolving precise sample weights of the Analar grade salts $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, $\text{K}_2\text{Cr}_2\text{O}_7$, $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ and



In the synthesized amides (PHMG-MA and PHMG-PA) on the average one molecule of appropriate anhydride was grafted on each 3.3 monomeric units of polyhexamethyleneguanidine.

The silica gel (Merck) with the specific surface area of 256 m²/g, pore size of 12 nm and particles diameter of 0.10–0.20 mm was used as a carrier.

Chemical binding of PHMG-MA and PHMG-PA to the silica surface was carried out in three stages. At the first stage, an amine-containing silica gel was obtained through the chemical modification of the surface with a solution of 3-aminopropyltriethoxysilane in toluene. An initial silica sample (70 g) was preliminarily dried at 200 °C for 2 h. Then the silica was placed in a three-necked round bottom reactor with a thermometer and a reflux condenser and suspended in 250 ml of absolute toluene, after which 14 ml of 3-aminopropyltriethoxysilane was added under constant stirring. The reaction mixture was refluxed at the toluene boiling temperature for 2 h. The amine-containing silica (aminosilica) thus obtained was then filtered and after being

NH_4VO_3 using the method described in [30]. Working solutions were prepared from the starting ones immediately before the experiments. The necessary solutions of acids were prepared from fixanal concentrates.

Synthesis of adsorbent. Amides used for the surface modification were synthesized by way of interaction of polyhexamethyleneguanidine hydrochloride ($M_w \approx 10000$) with anhydrides of maleic or *o*-phthalic acids as was described in the paper [31]. The amides thus obtained can be presented schematically through the following formula:

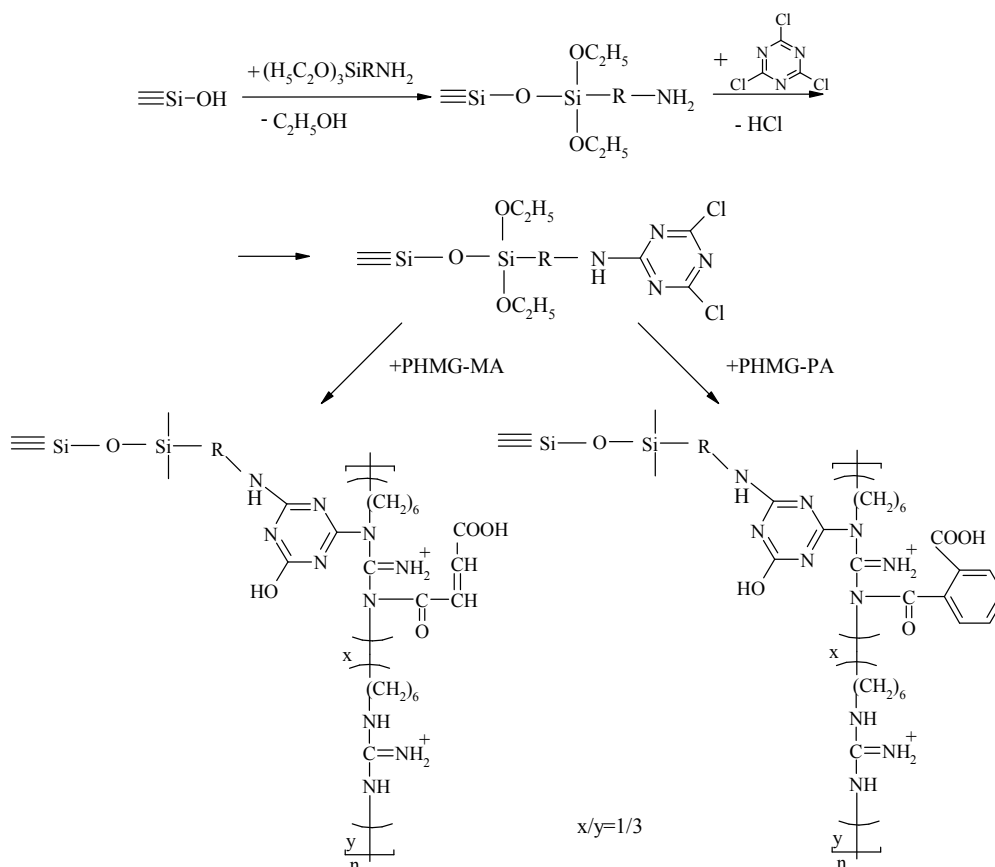
washed with 50 ml toluene 5 times was dried in vacuum at 100–110 °C. The concentration of grafted amino groups (0.8 mmol/g) was estimated using titrimetry for hydrochloric acid residues with sodium hydroxide.

At the second stage, the activation of the aminosilica surface with cyanuric chloride (2,4,6-trichloro-*symm*-triazine) was performed [32]: 70 g of aminosilica was suspended in 100 ml of dioxane in a three-necked reactor with a mechanical mixer. Then 330 ml of 5 % solution of cyanuric chloride in dioxane was added and the suspension was stirred at room temperature for 0.5 h. The product obtained was washed from surplus of cyanuric chloride 5 times with 50 ml dioxane and then dried in vacuum at 100 °C.

The goal of the third stage was to chemically bind PHMG-MA or PHMG-PA with the modified silica surface via interaction of immobilized cyanuric chloride with the polymeric macromolecules: the 75 g of activated aminosilica obtained at the second stage was placed into the reactor and 200 ml of water solution containing 15 g of polymer was added with the mixture being stirred for 1 h. Then the

synthesized adsorbents were filtered and dried at room temperature.

A general scheme of chemical transformations in the surface layer can be presented in the following way:



Under such conditions the incorporation and activation of amino groups on the outer surface as well as in the pores of the used mesoporous silica occurs without significant difficulties. Although the presence of mesopores can complicate the uniform adsorption of the polymer, especially on the pores surface, the use of silica gel is justified by a significant reduction in duration of filtration in comparison with highly dispersed nonporous silica preparations. At the same time for the immobilization of water-soluble polymer, it is sufficient to ensure its covalent binding to the accessible parts of a carrier.

IR-spectra. IR-spectra of the synthesized adsorbents were investigated to confirm the immobilization of PHMG-MA and PHMG-PA on the silica surface. Spectra were registered using a Nicolet Nexus 470 FT-IR spectrometer. The presence of anchored amides was identified in the range of $1750\text{--}1765\text{ cm}^{-1}$ by characteristic bands corresponding to the stretching vibrations $\text{C}=\text{O}$ of carbonyl groups as well as absorption bands in the

range of $1630\text{--}1690\text{ cm}^{-1}$ (amide I band) and $1590\text{--}1620\text{ cm}^{-1}$ (amide II band) which are typical for carbonyl groups of amide [33].

Amounts of bound polymers. Amounts of bound PHMG-MA and PHMG-FA were determined by thermogravimetry and titrimetry. According to gravimetric data, the amount of bound PHMG-MA in the synthesized adsorbent was 150 mg/g and in the case of silica with immobilized PHMG-PA it was 75 mg/g SiO_2 . According to acid-base titration [34], the concentrations of carboxylic groups are 0.15 mmol/g for silica with bound PHMG-MA and 0.09 mmol/g for silica with immobilized PHMG-PA.

Adsorption of metal-containing anions. The degree of ions adsorption on the surface of modified silica (%) was calculated using the following formula:

$$R = (m_{\text{ads}}/m_0) \cdot 100\% = (m_0 - m)/m_0 \cdot 100\%$$

where m_o is the weight of introduced anion, m_{ads} is the weight of adsorbed anion, m is the weight of anion in the equilibrium solution, calculated as $m = C \cdot V$ (C is an equilibrium concentration and V is an equilibrium volume).

Photometric measurements of equilibrium concentrations of Cr(IV), Mo(VI), W(VI) and V(V) anions were made using spectrophotometer SF-46 (LOMO, Russia) in a quartz cell with the path length of 10 mm at 540 nm for Cr(IV), 470 nm for Mo(VI), 610 nm for W(VI) and 490 nm for V(V) according to methods presented in [35, 36].

X-ray-fluorescence analysis. An X-ray-fluorescence analysis was made using a multichannel X-ray-fluorescence spectrometer ElvaX (Elvatex, Ukraine). Air-dried samples of chemically modified silica with grafted PHMG-MA weighing 0.2 g each with different quantities of vanadium or molybdenum previously adsorbed were used for measurements. The

optimal conditions for metal detection were as follows: an X-ray tube with the voltage of 45 kV, exposure time of 250 s for microquantities and of 150 s for milligram quantities of the analyte, with current intensities in determination of V and Mo being 86 and 30 μ A, respectively.

RESULTS

Dependence of the degree of adsorption on the pH solution. Studies of adsorption properties of silica with chemically bound polymers began from the determination of the optimal value of medium acidity in which the maximum degree of extraction of a chosen anion was achieved. The conditions of the experiment were as follows: the weight of the adsorbent was 0.1 g, the volume of the working solution was 25 ml, the metal mass in the initial solution was 100 μ g (10 mg for tungsten), and the contact time was 24 h. The results are summarized in the Table 1.

Table 1. Dependence of adsorption degree on the solution nature and pH for extraction of metal-containing anions from V and VI groups of the Periodic Table by silicas with chemically bound PHMG-MA and PHMG-PA

pH	Adsorption, %							
	V(V)		W(VI)		Mo(VI)		Cr(VI)	
	Silica with chemically bound							
	PHMG-MA	PHMG-PA	PHMG-MA	PHMG-PA	PHMG-MA	PHMG-PA	PHMG-MA	PHMG-PA
1.0 (hydrochloric acid)	18.8	60.0	83.8	83.2	30.0	0	71.4	87.5
1.7 (oxalate buffer)	42.5	47.5	–	–	97.0 [Mo ₆ O ₂₁] ⁶⁻	55.0	82.2	99.9 [Cr ₂ O ₇] ²⁻
4.0 (phthalate buffer)	99.9 VO ³⁻	92.5	99.9 [H ₂ W ₁₂ O ₄₀] ⁶⁻ [W ₄ O ₁₃] ²⁻	99.9	85.0	80.0	35.3	45.0
5.5 (distilled water)	99.9 VO ³⁻ [V ₄ O ₁₂] ⁴⁻	99.9	62.1	83.5	98.0 MoO ₄ ²⁻	75.5	96.5	92.5
6.9 (phosphate buffer)	80.0	60.0	–	–	15.0	20.0	8.3	15.0
8.0 (ammonium-acetate buffer)	99.9 VO ³⁻ [HVO ₄] ²⁻	50.0	60.0	76.8	76.0	55.0	32.5	25.0
9.1 (tetraborate buffer)	55.0	35.0	48.6	61.7	48.5	57.0	73.5	10.0

As seen from Table 1, a quantitative extraction of W(VI) and maximum removal of Mo(VI) anions was observed in the slightly acidic medium for both of adsorbents. Under these conditions, tungsten anions in the solution exist as dodecatungstate ([H₂W₁₂O₄₀]⁶⁻) and tetratungstate ([W₄O₁₃]²⁻) ions [37, 38]. Silica with anchored amide of PHMG and maleic acid

shows a higher activity in adsorption of molybdate anions in comparison with bound amide of PHMG and *o*-phthalic acid. Both synthesized adsorbents quantitatively remove anions V(V) in the slightly acid environment. Silica with bound PHMG-MA has a wide range of quantitative adsorption vanadate ions: from slightly acidic to weakly alkaline media. For

Cr(VI) anions, silica with immobilized amide of PHMG and *o*-phthalic acid possesses a higher adsorption activity and quantitatively removes dichromate ions in the acidic medium.

From data shown in Table 1, the adsorption of Cr(VI) and Mo(VI) falls at pH = 6.9. These results could be explained by the influence of phosphate buffer solution. Molybdate and phosphate anions form heteropolyacids which are stable in acidic and weakly acidic media [39]. In the case of adsorption of chromate-anions it is necessary to take into account the competitive adsorption of different anions from the buffer solution. Silica with chemically immobilized PHMG was found to be able to adsorb phosphate anions strongly [25]. The competitive adsorption of these anions was also detected on other type of adsorbents [40]. So in these conditions silicas with chemically bound PHMG-MA and PHMG-PA show a higher affinity to the phosphate anions in comparison with the adsorption of chromate ions.

Therefore, the obtained chemically modified silicas show a high adsorption activity with respect to anions of elements from V and VI groups of the Periodic Table in the acidic (pH = 1.7) and the slightly acid (pH = 4.0) media where the maximum possible extraction of studied metal-containing anions was observed. The results obtained are very close to data on the adsorption of these oxoanions on the surface modified with N-(β -aminoethyl)- γ -aminopropyltriethoxysilane [38].

The standard deviations for all measurements are within 3–4 %.

Kinetic characteristics of adsorbents.

Conditions of the kinetic experiments were as follows: the weight of adsorbent was 0.1 g, the volume of working solution 25 ml and the mass of metal in the initial solution 100 mg (10 mg for W). The results of studies of the kinetic characteristics of the synthesized sorbents with respect to anions under research are shown in Figs. 1 and 2.

Kinetic parameters of the obtained composites are similar to a polymeric adsorbent than to an inorganic one, because the maximum possible extraction of the anions under study, with the exception of tungsten, occurs within 1–1.5 h. A comparison of the kinetic curves shows that the adsorption values of tungstate and vanadate ions are similar for both sorbents, but they differ substantially for molybdate ions.

These results may testify the difference in the mechanism of molybdate ions adsorption.

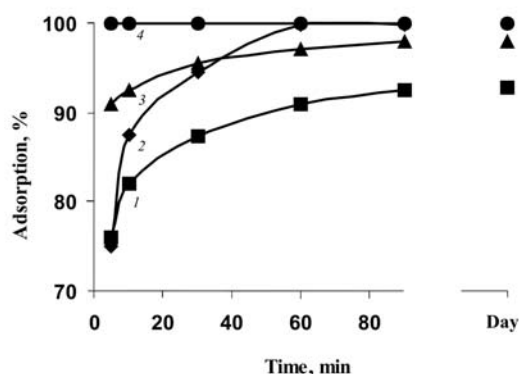


Fig. 1. Kinetics of removal of metal-containing anions by silica with chemically bound PHMG-MA in the static adsorption mode: 1 – Cr(VI), pH = 7; 2 – V(V), pH = 7; 3 – Mo(VI), pH = 7; 4 – W(VI), pH = 4

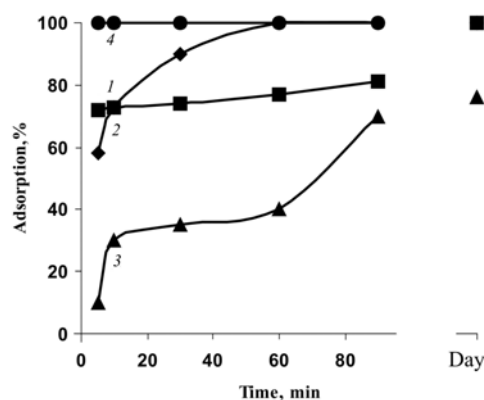


Fig. 2. Kinetics of removal of metal-containing anions by silica with chemically bound PHMG-PA in the static adsorption mode: 1 – Cr(VI), pH = 1.7; 2 – V(V), pH = 7; 3 – Mo(VI), pH = 7; 4 – W(VI), pH = 4

Adsorption capacity of synthesized adsorbents. For estimation of the adsorption capacity of silicas with chemically bound PHMG-MA and PHMG-PA the adsorption isotherms of Mo(VI)-, W(VI)-, Cr(VI)-, and V(V)-containing anions have been investigated. Experiments were carried out with initial quantities of metals in the solution from 0.02 up to 30.44 mmol/l, the volume of working solution is 25 ml, weight of adsorbent is 0.1 g. Typical isotherms for adsorption of Cr(VI) are shown in Figs. 3, 4. The presented curves have the Langmuir isotherm mode. The same results were obtained for isotherms of other studied metal-containing anions.

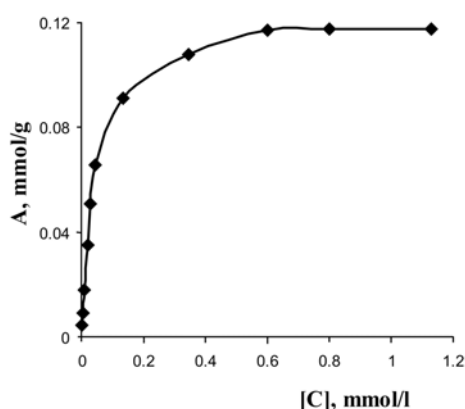


Fig. 3. Adsorption isotherm of Cr(VI) anions by silica with chemically bound PHMG-MA (pH = 5.5)

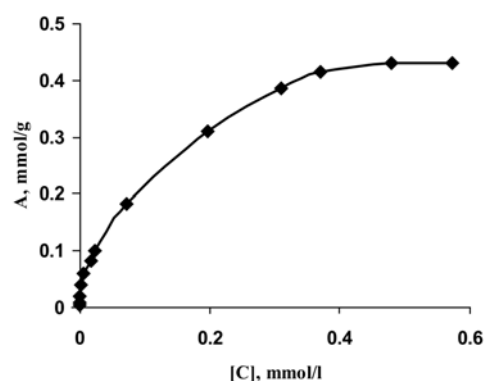


Fig. 4. Adsorption isotherm of Cr(VI) anions by silica with chemically bound PHMG-PA (pH = 1.7)

Table 2. Adsorption capacity of synthesized adsorbents with respect to metal-containing anions

Anion	V(V)		Cr(VI)		Mo(VI)		W(VI)	
	Silica with chemically bound							
Adsorbent	PHMG-MA	PHMG-PA	PHMG-MA	PHMG-PA	PHMG-MA	PHMG-PA	PHMG-MA	PHMG-PA
adsorption capacity, mmol/g	0.44	0.41	0.12	0.43	0.55	0.54	4.17	6.00
color of adsorption complexes	yellow	yellow	orange	from grey to grey-orange	light-green	blue-green	white	white

Adsorption capacities calculated from isotherm data are summarized in the Table 2. It is evident from these data that sorption capacities of both adsorbents with respect to vanadate and molybdate ions are practically equal. In the case of tungstate and chromate ions adsorption the silica with immobilized PHMG-PA exhibits higher adsorption capacity.

The synthesized adsorbents show greater sorption capacity with respect to anions of molybdenum and tungsten in comparison with modified silicas with other immobilized nitrogen-containing polymers [12–14].

Spectral studies of adsorption complexes of metal-containing anions with PHMG-PA anchored on the silica surface. Complexes of Mo(VI) anions adsorbed on silica with chemically bound PHMG-PA from aqueous solution (without further addition of buffer solutions) have blue-green color. As the amount of adsorbed metal is increased, the intensity of coloration is enhanced.

Diffuse reflectance UV-Vis spectra have been registered to clarify an oxidation degree of molybdenum in the ion associates with immobilized PHMG-PA. In accordance with

spectral data (Fig. 5), the intense absorption band with maximum at 470 nm and less intense absorption band with maximum at 710 nm in the visible region were observed.

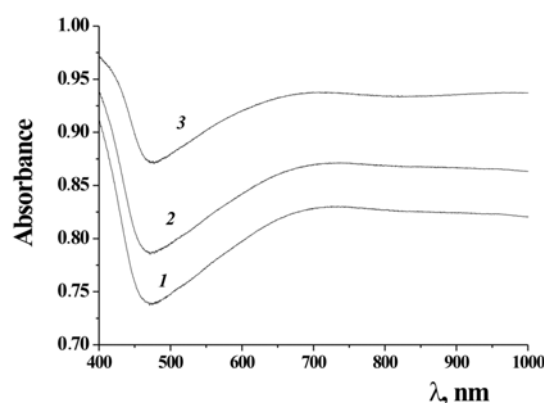


Fig. 5. Diffuse reflectance spectra of silica with chemically bound PHMG-PA after adsorption of 7.5, 10 and 38.5 mg/g sorbent of molybdenum (1–3, respectively)

Based on results [41] one would expect that molybdenum in ion associate exists in the form of pentavalent molybdenyl. This is due to the

fact that side redox processes of transition of hexavalent molybdenum in pentavalent state occurs during adsorption.

Ion associates of immobilized PHMG-PA with anions of chromium obtained from aqueous solutions of potassium dichromate at pH = 1.7 (on the background of oxalate buffer solution) change their color from gray to gray-orange. It has been known that gray color is the typical feature of trivalent chromium aqua complexes. As seen from diffuse reflectance spectra (Fig. 6), three absorption bands are observed for these associates. Intense absorption band in the visible region with maximum absorption at 580 nm belongs to the charge transfer bands of metal-ligand and the least intense band with maximum absorption at 700 nm can be attributed to *d-d* transitions of Cr(III).

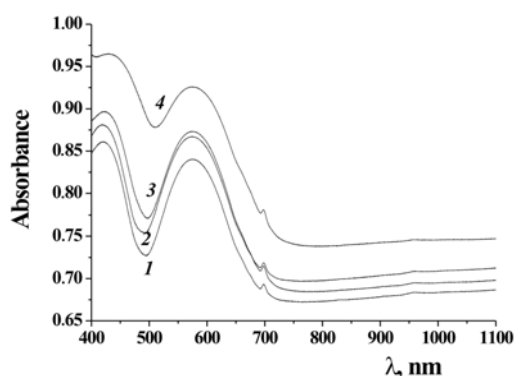


Fig. 6. Diffuse reflectance spectra of silica with chemically bound PHMG-PA after adsorption of 5.5, 7.5, 8.5 and 16 mg/g sorbent of chromium (1–4, respectively)

Adsorption-X-ray-fluorescence determination of microquantities of vanadium and molybdenum adsorbed on silica with chemically bound PHMG-MA. The ability of the synthesized composite to adsorb quantitatively V(V) and Mo(VI) anions can be effectively applied for their solid-phase extraction. Quantitative analysis of the relevant metals after their preconcentration can be performed directly in the adsorbent phase by various physical methods, including X-ray-fluorescence spectrometry. Dependences of intensity of characteristic K_{α} -lines of vanadium and molybdenum on quantities of these metals in the adsorbent phase were obtained (Fig. 7).

These dependences were rectilinear over the range of milligram amounts of molybdenum (from 0.5 up to 40 mg/g sorbent) and microgram

quantities of vanadium (from 0.5 up to 18 mg/g sorbent). Detection limit for both metals was 20 μ g.

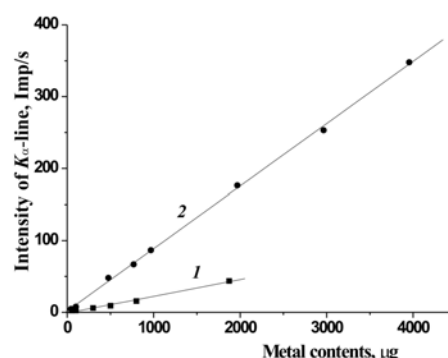


Fig. 7. Dependence of K_{α} -line intensity of characteristic X-ray radiation of metal on its contents in the adsorbent phase:

1 – vanadium ($R = 0.998$);
2 – molybdenum ($R = 0.999$)

CONCLUSIONS

Chemical binding of amides of polyhexamethyleneguanidine and maleic or *o*-phthalic acids were carried out on the surface of amino-containing silica activated with cyanuric chloride.

Concentrations of bound polymers according to thermogravimetric analysis were 75 mg per 1 g of carrier for amide of *o*-phthalic acid and 140 mg/g for amide of maleic acid. Synthesized modified silicas were found to show high adsorption activity with respect to anions of metals of V and VI groups of the Periodic Table in aqueous solution at the neutral pH. Quantitative adsorption of Cr(VI) and W(VI) anions has been observed in the acidic and weakly-acidic media, respectively. Silicas with chemically bound PHMG-MA and PHMG-PA have kinetic characteristics which are similar to polymeric adsorbents. Equilibrium is attained for 1–1.5 h, with the exception of a fast adsorption of tungsten(VI) anions. Sorption capacities of silicas with immobilized PHMG-MA and PHMG-PA with respect to vanadate and molybdate ions are practically equal (0.41–0.55 mmol/g). Silica with bound PHMG-PA adsorbs Cr(VI) anions better than carrier with immobilized PHMG-MA. Both obtained adsorbents displayed a high affinity to W-containing anions (4–6 mmol/g).

In accordance with the data of UV-Vis diffuse reflectance spectroscopy, adsorbed molybdenum ions on surface of silica with bound PHMG-PA are in the form of molybdenyl-ions, and reduction Cr(VI) to Cr(III) takes place during adsorption of bichromate-ions. The possibilities of quantitative determination of V and Mo in phase of adsorbent using X-ray-fluorescence spectroscopy were shown after preconcentration on the silica with bound PHMG-MA.

REFERENCES

1. *Leyden D.E., Luttrell G.H., Sloan A.E. et al.* Characterization and application of silylated substrates for the preconcentration of cations // *Anal. Chim. Acta.* – 1976. – V. 84, N 1. – P. 97–108.
2. *Biernat J.F., Konieczka P., Tarbet B.J. et al.* Complexing and chelating agents immobilized on silica gel and related materials and their application for sorption of inorganic species // *Separ. Purif. Methods.* – 1994. – V. 23, N 2. – P. 77–348.
3. *Zaitsev V.N.* Complexing Silica: Synthesis, Structure of the Grafted Layer and Surface Chemistry. – Khar'kov: Pholio, 1997. – 240 p. (in Russian).
4. *Huang X., Chang X., He Q. et al.* Tris(2-aminoethyl) amine functionalized silica gel for solid-phase extraction and preconcentration of Cr(III), Cd(II) and Pb(II) from waters // *J. Hazard. Mater.* – 2008. – V. 157, N 1. – P. 154–160.
5. *Pereira A.S., Ferreira G., Caetano L. et al.* Preconcentration and determination of Cu(II) in a fresh water sample using modified silica gel as a solid-phase extraction adsorbent // *J. Hazard. Mater.* – 2010. – V. 175, N 1–3. – P. 399–403.
6. *Ekinci C., Köklü Ü.* Determination of vanadium, manganese, silver and lead by graphite furnace atomic absorption spectrometry after preconcentration on silica-gel modified with 3-aminopropyltriethoxysilane // *Spectrochim. Acta, Part B.* – 2000. – V. 55, N 9. – P. 1491–1495.
7. *Zolotov Yu.A., Tsysin G.I., Morosanova E.I. et al.* Sorption preconcentration of microcomponents for chemical analysis // *Russ. Chem. Rev.* – 2005. – V. 74, N 1. – P. 37–60.
8. *Krokhin O.V., Smolenkov A.D., Svintsova N.V. et al.* Modified silica as a stationary phase for ion chromatography // *J. Chromatogr. A.* – 1995. – V. 706, N 1–2. – P. 93–98.
9. *Pirogov A.V., Svintsova N.V., Kuzina O.V. et al.* Silicas modified by polyelectrolyte complexes for the ion chromatography of anionic complexes of transition metals // *Fresenius J. Anal. Chem.* – 1998. – V. 361, N 3. – P. 288–293.
10. *Svintsova N.V., Smolenkov A.D., Krokhin O.V. et al.* Use of new surface-modified sorbents based on silica gel for the determination of anionic transition metal complexes by ion chromatography // *J. Anal. Chem.* – 1998. – V. 53, N 4. – P. 347–350.
11. *Weiss J., Jensen D.* Modern stationary phases for ion chromatography // *Anal. Bioanal. Chem.* – 2003. – V. 375, N 1. – P. 81–98.
12. *Polishchuk L.N., Yanovska E.S., Yanishpolskii V.V. et al.* Sorption of Mo(VI), W(VI), Cr(VI), and V(V) anions on a silica gel modified with immobilized polyionene // *Russ. J. Appl. Chem.* – 2007. – V. 80, N 9. – P. 1590–1593.
13. *Tertykh V.A., Polishchuk L.M., Yanovska E.S., Dadashev A.D.* Concentration of anions by silica adsorbents with immobilized nitrogen-containing polymers // *Adsorpt. Sci. Technol.* – 2008. – V. 26, N 1–2. – P. 59–68.
14. *Tertykh V., Polishchuk L., Yanishpolskii V. et al.* Adsorption properties of functional silicas towards some toxic metal ions in water solutions // In: J.P. Mota, S. Lyubchik, Eds. *Adsorption Processes for Environmental Protection and Security, NATO Science for Peace and Security Series – C: Environmental Security.* – Dordrecht: Springer, 2008. – P. 119–132.
15. *Gembitskii P.A., Vointseva I.I.* Polymeric Biocidal Preparation of Polyhexamethyleneguanidine – Zaporozh'e: Poligraph, 1998. – 44 p. (in Russian).
16. *Ampilogova N.A., Karavan V.S., Moskalenko M.A., Nikiforov V.A.* Synthesis of guanidine salts and possibilities of their using as anion-exchangers // *J. Anal. Chem.* – 1989. – V. 44, N 4. – P. 620–623.
17. *Nizhnik T.Yu., Baranova A.I., Rokitskaya O.B., Nizhnik V.V.* Complexing of copper ions with polyhexamethyleneguanidine in aqueous solution // *Zh. Khromatographichnogo Tovarystva.* – 2004. – V. 4, N 2. – P. 16–25 (in Russian).
18. *Nizhnik T.Yu., Nizhnik V.V., Malysheva M.L., Astrelin I.M.* Complexing of polyhexamethyleneguanidine hydrochloride with cobalt ions // *Voprosy khimii i khimicheskoi tekhnologii.* – 2006. – N 6. – P. 120–124 (in Ukrainian).

19. *Nikashina V.A., Gembitskii P.A., Kats E.M. et al.* Organomineral sorbents based on clinoptilolite-containing tuffs // *Russ. Chem. Bull.* – 1994. – V. 43, N 9. – P. 1462–1465.
20. *Nikashina V.A., Kats E.M., Gembitskii P.A.* Organomineral sorbents based on clinoptilolite-containing tuffs // *Russ. Chem. Bull.* – 1994. – V. 43, N 9. – P. 1466–1468.
21. *Misaelides P., Nikashina V., Godelitsas A. et al.* Sorption of As(V)-anions from aqueous solutions by organo-modified natural zeolitic materials // *J. Radioanal. Nucl. Chem.* – 1998. – V. 227, N 1–2. – P. 183–186.
22. *Misaelides P., Zamboulis D., Sarridis Pr. et al.* Chromium(VI) uptake by polyhexamethyleneguanidine-modified natural zeolitic materials // *Microporous Meso-porous Mater.* – 2008. – V. 108, N 1–3. – P. 162–167.
23. *Yanovska E.S., Dadashev A.D., Tertykh V.A.* Inorganic anion-exchanger based on silica with grafted polyhexamethyleneguanidine hydrochloride // *Funct. Mater.* – 2009. – V. 16, N 1. – P. 105–109.
24. *Yanovska E.S., Dadashev A.D., Tertykh V.A.* Complexing of transition metal cations with polyhexamethyleneguanidine hydrochloride chemically anchored on silica gel surface // *Ukr. Khim. Zhurn.* – 2009. – V. 75, N 2. – P. 69–74 (in Ukrainian).
25. *Dadashev A.D., Yanovska E.S., Tertykh V.A.* Application of silica with grafted polyhexamethyleneguanidine hydrochloride in concentration and determination of transition metal cations and metal-containing anions // *Naukovi zapysky NaUKMA, khim. nauky i tekhnol.* – 2009. – V. 92. – P. 23–27 (in Ukrainian).
26. *Losev V.N., Didukh S.L., Trofimchuk A.K., Leshchenko V.N.* Palladium(II) and cobalt(II) sorption by silica gel sequentially modified by polyhexamethyleneguanidine and a nitroso-R salt // *Mendeleev Commun.* – 2009. – V. 19, N 3. – P. 167–169.
27. *Trofimchuk A.K., Maglyovana T.V., Leshchenko V.N.* Development of the analytic form of reagents on the basis of silica gel impregnated with polyhexamethyleneguanidine chloride // *Polish J. Chem.* – 2009. – V. 82, N 1. – P. 453–460.
28. *Losev V.N., Didukh C.L., Buiko E.V. et al.* Application of silica modified with polyhexamethyleneguanidine and 8-hydroxyquinoline-5-sulfur acid for concentration and sorption-atomic emission determination of metals in natural water // *Analitika i control.* – 2009. – V. 13, N 1. – P. 33–39 (in Russian).
29. *Dadashev A.D., Tertykh V.A., Yanovska E.S. et al.* Sorption of transition metals by silica gel with surface-fixed amide of maleic acid and polyhexamethyleneguanidine // *Russ. J. Appl. Chem.* – 2010. – V. 83, N 12. – P. 2110–2114.
30. *Korostylev P.P.* Preparation of Solutions for Chemical-Analytical Work. – Moscow: Nauka, 1964. – 399 p. (in Russian).
31. *Boiko V.V., Dmitrieva T.V., Bortnitskii V.I. et al.* Mass-spectrometric study of thermal destruction of carboxymethyl derivatives of polyguanidine hydrochlorides // *Polimernyi zhurnal.* – 2009. – V. 31, N 2. – P. 119–125 (in Russian).
32. *Tertykh V.A., Yanishpolskii V.V.* Adsorption and chemisorption of enzymes and other natural macromolecules on silicas // In: *E. Papirer, Ed. Adsorption on Silicas.* – New York: Marcel Dekker, 2000. – P. 523–564.
33. *Gordon A.J., Ford R.A.* The Chemist's Companion. – New York: Wiley-Interscience, 1972. – 541 p.
34. *Puziy A.M., Poddubnaya O.I., Kochkin Yu.N. et al.* Acid properties of phosphoric acid activated carbons and their catalytic behavior in ethyl-tert-butyl ether synthesis // *Carbon.* – 2010. – V. 48, N 3. – P. 706–713.
35. *Marchenko Z.* Photometric Determination of Elements. – Moscow: Mir, 1971. – 502 p. (in Russian).
36. *Busev A.I., Ivanov V.M., Sokolova T.A.* Analytical Chemistry of Tungsten. – Moscow: Nauka, 1976. – 240 p. (in Russian).
37. *Ripan R., Ceteanu I.* Inorganic Chemistry. – Moscow: Mir, 1972. – 502 p. (in Russian).
38. *Leyden D.E., Luttrell G.H., Nonidez W.K., Werho D.B.* Preconcentration of certain anions using reagents immobilized via silylation // *Anal. Chem.* – 1976. – V. 48, N 1. – P. 67–70.
39. *Fedorov A.A.* Analytical Chemistry of Phosphorus. – Moscow: Nauka, 1974. – 220 p. (in Russian).
40. *Foster N. S., Amonette J.E., Autrey S.T.* In situ detection of chromate using photoacoustic spectroscopy // *Appl. Spectrosc.* – 1999. – V. 53, N 6. – P. 735–740.
41. *Lever A.B.P.* Inorganic Electronic Spectroscopy. – Amsterdam: Elsevier, 1968. – 863 p.

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Йонообмінні властивості модифікованого силікагелю з закріпленими амідами полігексаметиленгуанідину та малеїнової або *o*-фталевої кислот

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*Аміди полігексаметиленгуанідину та малеїнової або *o*-фталевої кислот було хімічно закріплено на поверхні силікагелю. Досліджено адсорбційну здатність модифікованих силікагелів щодо $V(V)$ -, $Cr(VI)$ -, $Mo(VI)$ - та $W(VI)$ -вмісних аніонів. Знайдено, що обидва сорбенти виявляють достатньо високу адсорбційну активність у кислому та слабкокислому середовищі. За кінетичними характеристиками одержані композиції подібні до полімерних адсорбентів. Під час адсорбції на силікагелі з хімічно закріпленим амідом полігексаметиленгуанідину та *o*-фталевої кислоти спостерігається відновлення йонів $Mo(VI)$ та $Cr(VI)$. Показана можливість кількісного визначення мікрокількостей досліджених металів у фазі адсорбенту з використанням рентгенофлуоресцентного аналізу після твердофазної екстракції аніонів з розчину.*

Ионообменные свойства модифицированного силикагеля с закрепленными амидами полигексаметиленгуанидина и малеиновой или *o*-фталевой кислот

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*Амиды полигексаметиленгуанидина и малеиновой или *o*-фталевой кислот были химически закреплены на поверхности силикагеля. Изучена адсорбционная способность модифицированных силикагелей по отношению к $V(V)$ -, $Cr(VI)$ -, $Mo(VI)$ - и $W(VI)$ -содержащих анионов. Найдено, что оба сорбента имеют достаточно высокую адсорбционную активность в кислой и слабкокислой среде. По кинетическим характеристикам полученные композиции подобны полимерным адсорбентам. При адсорбции на силикагеле с химически закрепленным амидом полигексаметиленгуанидина и *o*-фталевой кислоты наблюдается восстановление ионов $Mo(VI)$ и $Cr(VI)$. Показана возможность количественного определения микроколичеств изученных металлов в фазе адсорбента с использованием рентгенофлуоресцентного анализа после твердофазной экстракции анионов из раствора.*