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Chitosan Immobilized on Silica Surface for Wastewater Treatment

Tetyana BUDNYAK [1] *, **Valentin TERTYKH** [1], **Elina YANOVSKA** [2]

[1] *Chuiko Institute of Surface Chemistry of National Academy of Sciences of Ukraine, 17 General Naumov Str., 03164 Kyiv*
[2] *Taras Shevchenko National University of Kyiv, 62a Volodymyrska Str., 01033 Kyiv, Ukraine*

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Adsorbents of natural origin are widely used for industrial wastewater treatment in order to replace current costly methods of heavy metals removing from solutions. For that purpose, immobilization of chitosan on the silica gel surface by crosslinking of adsorbed biopolymer with glutaraldehyde was carried out. Anchorage of chitosan on the silica surface was confirmed by IR spectroscopy. Concentration of immobilized chitosan was estimated using thermogravimetric analysis. The adsorption of microquantities of Zn(II), Cu(II), Cd(II), Pb(II), Fe(III), V(V) and Mo(VI) ions from aqueous solutions by obtained composite has been studied. The highest sorption capacities were observed with respect to zinc (0.46 mmol/g), molybdenum- and vanadium-containing ions (0.31 mmol/g). Diffuse reflectance electronic spectra of samples with different content of adsorbed metal and kinetic adsorption characteristics of the composite adsorbent were estimated.

Keywords: adsorption, chitosan, silica, toxic metals removal, wastewater treatment.

1. INTRODUCTION

Polymers with the expressed ion-exchanging and complexing properties are widely used recently to improve the sorption properties of mineral adsorbents. In this respect, natural biopolymer chitosan attracts attention. Properties of inorganic matrix of composites mineral carrier-chitosan could be improved by valuable features of a polymer. In particular, chitosan has proper biocompatibility, high adhesion to the surface, wide range of pH-stability, ability to biodegradation, nontoxicity, complexing properties. Alternatively, mineral carriers are characterized by the advanced surface area, heat resistance, stability to the microorganism's attack and proper adsorption kinetics. Recent studies have shown that composites silica-chitosan [1 – 4] and biosorbents based on chitosan and various natural minerals [5 – 12] can be used for heavy metals extraction and its preconcentration from solutions. However, there is necessity for systematic studies of adsorption characteristics with respect to cations and metal-containing anions depending on the nature and pH of medium in order to determine the optimal conditions of use and the sorption capacity of composites chitosan-mineral sorbents.

Chitosan and its derivatives was found to show activity towards adsorption of zinc(II), copper(II), cadmium(II), lead(II), iron(III), vanadium(V) and molybdenum(VI) ions [13 – 15]. In our work the adsorption properties of chitosan immobilized on the silica surface with respect to these ions have been studied.

2. EXPERIMENTAL DETAILS

Silica gel with a specific surface area of 256 m^2/g, particle size of 0.1 mm – 0.2 mm and an average pore size of 12 nm (Merck) was impregnated by chitosan solution (Sigma Aldrich, N 417 963) with a molecular weight from 190,000 Da to 370,000 Da, degree of deacetylation – not less than 75 % and solubility 10 mg/ml. For this, 20 g of silica and 285 ml of 7 mg/ml chitosan solution in acetic acid (pH 2.6) were putted in flat-bottom flask and mixed by the magnetic stirrer MM-5 for 2 h. The obtained substance was dried at 50 °C.

Chitosan has a high affinity to the surface due to the interaction between part of protonated amino groups of polymer and dissociated hydroxyl groups of silica, which are formed in aqueous solution (Fig. 1).

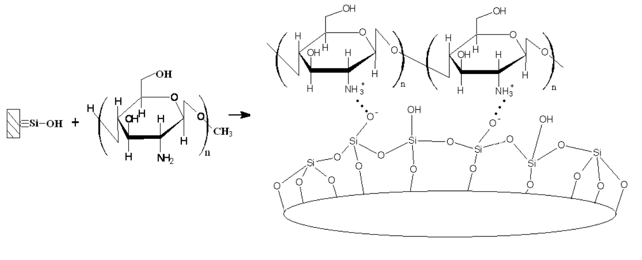

Fig. 1. The scheme of interaction between silica and chitosan

Lateral crosslinking of adsorbed polymer by glutaraldehyde was performed in order to better consolidate the surface layer, which is important in case of acidic solutions. For this, 10 ml of 0.025 % glutaraldehyde solution was added to the silica with the pre-adsorbed chitosan and stirred for 2 h. According to the calculations, used amount of dialdehyde support crosslinking about 5 % of aminogroups in the polymer layer. The obtained product was washed with repeated decantation and dried at 50 °C untill constant mass. In the result, silica-chitosan composite was synthesized with mass ratio chitosan : silica – 1 : 10.

The investigation of adsorption properties of the obtained composite with respect to Zn(II), Cu(II), Cd(II), Pb(II), Fe(III), V(V) and Mo(VI) ions was carried out in the static mode with periodic hand-stirring. For that samples of 0.1 g of synthesized adsorbent was contacted with 25 ml of solutions with different concentrations of

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* Corresponding author. Tel.: +38-0665631020, fax: +38-0444243567.
E-mail address: *tetyanabudnyak@yahoo.com* (T. Budnyak)

salts: $ZnCl_2$, $CuCl_2 \cdot 2H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Pb(NO_3)_2$, $FeCl_3$, NH_4VO_3, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, which were prepared under recommendations [16]. Photometric studies of equilibrium solutions were carried out according to the methods described in [17 – 19] using a SF-46 spectrophotometer (LOMO, Russia) with square cuvettes (optical path length $l = 1$ cm).

IR spectra of samples of initial materials and reaction products were recorded using IR spectrophotometer with Fourier transformation (Thermo Nicolet Nexus FT-IR, USA). For this purpose the samples was grinded in an agate mortar and pressed with KBr. The concentration of chitosan on the surface of silica gel was determined by thermogravimetric method on the derivatograph Q-1500 MOM (Hungary) with the computer data registration at the temperatures range 15 °C – 1000 °C. Samples heating rate was 10 degrees/min. DTA, TG and DTG curves were recorded simultaneously. Diffuse reflectance electronic spectra were obtained by spectrophotometer Specord-40.

The degree of adsorption (R) was calculated using the formula:

$$R = (m_{ads}/m_0) \cdot 100\ \% = (m_0 - m)/m_0 \cdot 100\ \%, \qquad (1)$$

where m_0 is the weight of the metal in the initial solution, m_{ads} is the mass of adsorbed metal, m is the mass of metal in solution after adsorption equilibrium, which was calculated as $m = C \cdot V$, where C is the equilibrium concentration of metal and V is the volume of equilibrium solution.

3. RESULTS AND DISCUSSION

To ascertain the immobilization of chitosan onto the surface of mesoporous silica, FT-IR spectroscopy was employed to characterize initial chitosan, silica and chitosan-modified silica. Similar features were seen for initial chitosan and silica, as well as unmodified hybrid materials as was reported earlier [3, 20], i. e., bands at 1700 cm^{-1} and 1550 cm^{-1} in the spectrum of chitosan (Fig. 2, curve 1) confirm the presence amino groups in the initial polymer.

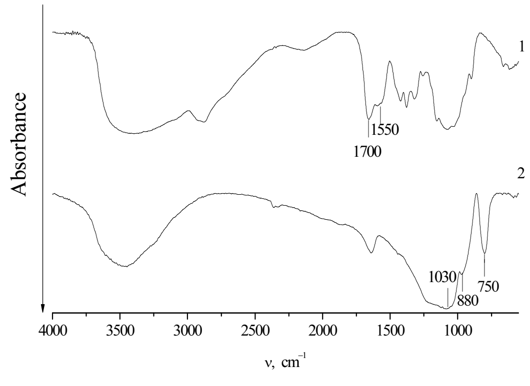


Fig. 2. FTIR spectra of chitosan (1) and silica (2)

The silica spectrum showed characteristic silicon oxide broad bands at 750, 880 and 1030 cm^{-1} corresponding to symmetric Si–O, Si–OH bonds and asymmetric Si-O-Si bonds stretching vibrations, respectively, due to the silicon oxide polymeric network (Fig. 2, curve 2). According to IR spectrum of the silica-chitosan composite (Fig. 3) intensive absorbance at 1530 cm^{-1}, which corresponds to the deformation vibrations of N–H of the protonated amino groups and the band at 1650 cm^{-1}, which describes azomethine bonds formed after glutaraldehyde treatment, are observed.

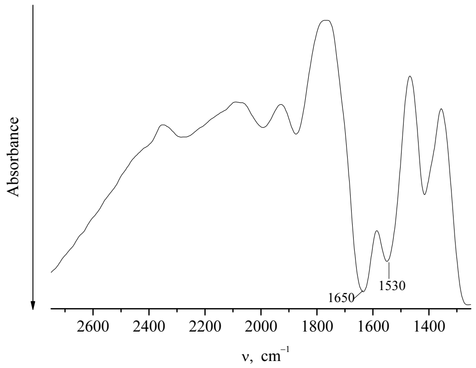
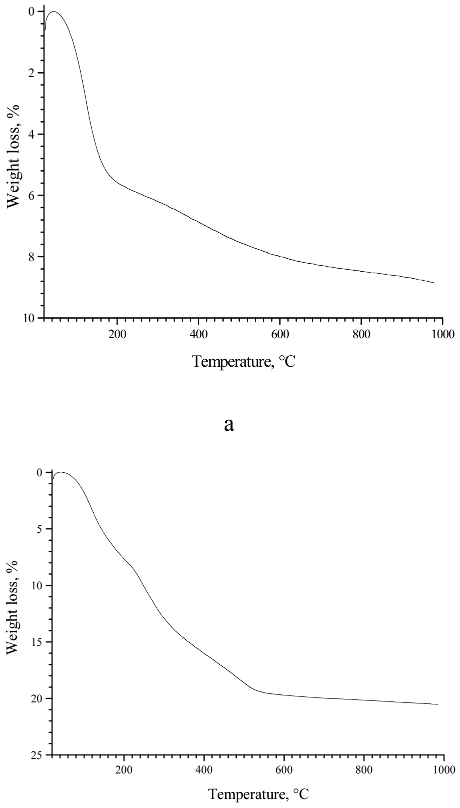


Fig. 3. FTIR spectrum of obtained silica gel-chitosan composite

The thermogravimetric analysis (hereinafter – TG) of silica and synthesized composite were conducted in order to determine the concentration of immobilized chitosan on the composite surface (Fig. 4). The comparison of TG curves of SiO_2 and composite silica-chitosan shows that in the temperature range from 100 °C to 700 °C weight loss of the composite silica-chitosan, which is most likely caused by destruction of the organic component of the composite, is about 10 %. Comparing this value with the weight of chitosan, which has been taken for the composite synthesis, shows almost complete polymer anchorage on the silica surface.



a

b

Fig. 4. TG-curves of silica (a) and composite silica-chitosan (b)

According to literature data, chitosan has interesting adsorption properties towards to Zn(II), Cu(II), Cd(II), Pb(II), Fe(III), V(V) and Mo(VI) ions [1 – 15]. The investigation of sorption properties of the synthesized composite was started from the definition of optimal values of medium acidity in which the removal of the studied ions was highest. The dependences of degree of removal of examined ions by silica gel with immobilized chitosan on nature and acidity of the medium are summarized in Table 1.

Table 1. The degree of adsorption of Zn(II), Cu(II), Cd(II), Pb(II), Fe(III), V(V) and Mo(VI) ions as function of the medium acidity

Ion	Degree of adsorption, %				
	pH 1.0	pH 2.5	pH 5.1	Distilled water	pH 8.0
Zn(II)	54.37	71.00	87.12	89.14	95.94
Cu(II)	0.00	63.25	55.00	44.56	83.50
Cd(II)	0.00	65.34	12.70	15.57	14.13
Pb(II)	0.00	65.53	56.19	62.63	11.08
Fe(III)	22.65	48.54	85.76	72.01	91.42
V(V)	99.10	99.57	99.96	99.90	99.87
Mo(VI)	0.00	22.9	7.27	49.30	6.20

Note: experimental conditions: mass of sorbent – 0.1 g, volume of solution – 25 ml, weight of zinc, copper, cadmium, lead, iron in the original solution – 0.1 mg, weight of vanadium, molybdenum in the initial solution – 1 mg.

It can be seen from the obtained data that zinc(II) ions were adsorbed quite well in almost the entire range of acidity of the medium. However, the maximum degree of sorption of 100 mg of zinc by synthesized composite was about 96 % in slightly alkaline medium at pH 8.0, which generated by ammonium acetate buffer. Also 87 % – 89 % of Zn(II) cations were removed from the weakly acidic medium, created by acetate ions, at pH 5.1, and from distilled water. In strongly acidic conditions (pH 1.0, chloride ions) adsorption of these cations was only 54 %.

Similarly to Zn(II) ions, Cu(II) and Fe(III) ions were extracted effectively (84 % and 91 %) by synthesized composite at pH 8.0 in the ammonium acetate buffer. However, unlike cations Zn(II) and Fe(III), Cu(II) ions are not adsorbed in 0.1 M HCl medium and moderately removed in the presence of acetate ions: 63 % at pH 2.5; 55 % at pH 5.1 and 45 % from distilled water. In the similar conditions Fe(III) ions were adsorbed better: 49 % at pH 2.5, 86 % at pH 5.1 and 72 % from distilled water.

The similar adsorption activity as function of the medium acidity was demonstrated by the synthesized composite towards highly toxic Pb(II) and Cd(II) ions. These ions were adsorbed better from the acidic medium in the presence of acetate ions: 65 % at pH 2.5. But if Cd(II) ions were poorly removed at all other values of pH medium, the 63 % of Pb(II) ions were adsorbed from distilled water.

1 mg of V(V) anions are removed quantitatively by the surface of synthesized composite at all investigated pH range, whereas Mo(VI) anions were quantitatively adsorbed only from distilled water.

Thus, the synthesized composite showed adsorption activity with respect to the investigated ions at different pH ranges. The values of medium acidity, at which the maximum of adsorption activity of silica-chitosan composite for each of the studied ions were achieved, correspond to published data of complexation conditions of these ions with amino groups of chitosan in solutions.

The silica-supported chitosan did not show adsorption activity with respect to examined metal ions, except zinc, iron and vanadium in medium created by 0.1 M HCl.

Adsorption isotherms in the static mode for each ion were obtained for calculating the values of the adsorption capacity of the composite.

The synthesized composite quantitatively removed from 50 μg to 3 mg of zinc in the form of $[Zn(NH_3)_4]^{2+}$ ions in the slightly alkaline medium at pH 8.0, created by ammonium acetate buffer. It was found that at the same conditions the degree of sorption of $[Cu(NH_3)_4]^{2+}$ ions gradually decreased from 74 % for a solution containing 50 μg of metal, to 13 % for 2 mg of copper in the initial solution. The sorption capacity of the composite with respect to Fe(III) ions gradually decreased from 81 % for 50 μg to 5.5 % for 3 mg of the metal at initial solution in distilled water.

At pH 2.5 and pH 7.0 the degree of adsorption of lead in the form of $[Pb(H_2O)_4]^{2+}$ ions increased with increasing metal content in the initial solution from 50 μg to 700 μg. In a case of Cd(II) ions, adsorption increased in the range of initial weight of cadmium from 50 μg to 500 μg at pH 2.5.

It was shown that in the neutral aqueous medium 63 % of molybdate-ions MoO_4^{2-} are quantitatively adsorbed when the content of molybdenum in the initial solution ranging from 50 μg to 3 mg. Mixture of dodecavanadate-ions ($[V_{10}O_{28}]^{6-}$, $[HV_{10}O_{28}]^{5-}$ and $[H_2V_{10}O_{28}]^{4-}$) with initial masses of vanadium from 10 micrograms to 2 mg was quantitatively adsorbed under the same conditions. Adsorption capacity of the composite towards V(V) ions is 0.31 mmol/g.

Adsorption isotherms of all investigated ions belong to the *L*-type and can be characterized by areas of growing and maximum adsorption (Figs. 5, 6), which is typical for monomolecular adsorption. Obtained values of the adsorption capacity of the composite are shown in Table 2. The obtained data of the adsorption kinetics of synthesized composite towards Zn(II), Cu(II), Cd(II), Pb(II), Fe(III), V(V) and Mo(VI) ions are presented in Table 3 and Fig. 7. Analysis of these data shows that the maximum degree of adsorption of all studied ions by composite surface are achieved overnight. But the manifestation of the adsorption activity of the synthesized composite is observed within a few minutes of contact that allows one to attribute the kinetics characteristics of synthesized composite to inorganic adsorbents.

Sorption capacity and kinetic characteristics of the synthesized composite are congruous with those for other sorbents [1 – 15] and this composite can be useful for removing all studied ions.

Literature data do not contain sufficient information about diffuse reflectance electronic spectra (DRES) in case of investigation of heavy metal complexes with chitosan on silica surface. DRES of composite samples with different content of adsorbed Cu(II), V(V), Mo(VI), Zn(II), Pb(II) Cd(II) and Fe(III) were investigated for clarifying the metal binding sites among the adsorbent's functional groups.

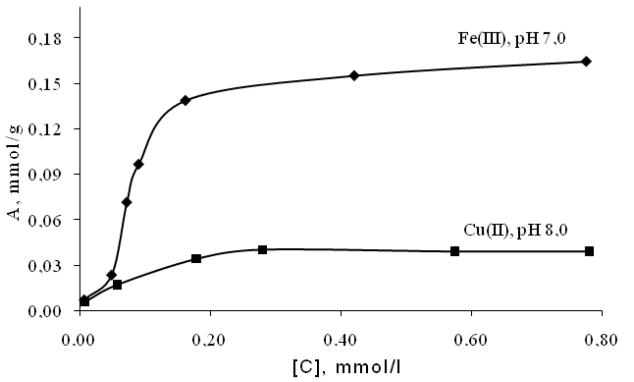


Fig. 5. Adsorption isotherms of Fe(III) and Cu(II) ions by silica-chitosan composite

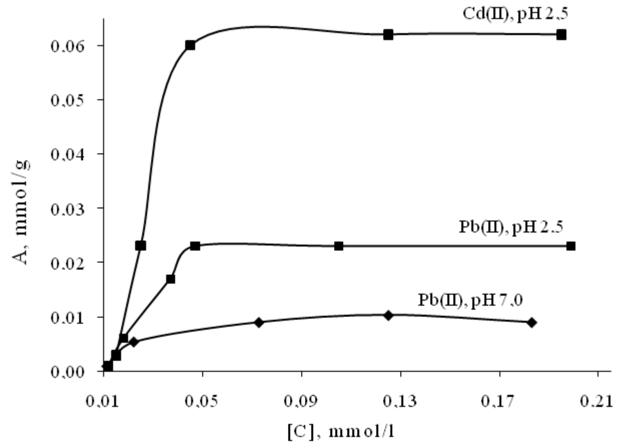


Fig. 6. Adsorption isotherms of Cd(II) and Pb(II) ions by silica-chitosan composite

Table 2. Adsorption capacity of chitosan immobilized on silica with respect to Zn(II), Cu(II), Cd(II), Pb(II), Fe(III), V(V) and Mo(VI) ions from initial solutions with various concentrations

Ion	pH	Adsorption capacity, mmol/g	Quantitative removal, mmol/g
Zn(II)	8.0	up to 0.46	up to 0.46
Cu(II)		0.05	0.01
Cd(II)	2.5	0.06	–
Pb(II)		0.03	–
Fe(III)	Distilled water	0.16	–
Pb(II)		0.01	–
V(V)		up to 0.31	up to 0.31
Mo(VI)		0.31	0.02

The electronic spectrum of the composite adsorbed 700 μg of copper (Fig. 8) shows three characteristic bands, which can be attributed correspondingly to interligand transitions of chitosan (450 nm) and to the bands of charge transition from ligand to the metal (610 nm and 680 nm).

The electronic spectra of the composite with different adsorbed amount of molybdenum ions (Fig. 9) have three characteristic bands, which can be attributed correspondingly to interligand transitions of chitosan (450 nm) and to the bands of charge transition from ligand to the metal (610 nm and 720 nm – 750 nm).

Table 3. Kinetics of Zn(II), Cu(II), Cd(II), Pb(II), Fe(III), V(V) and Mo(VI) ions removal by chitosan-silica composite in the static adsorption mode

Ion	The degree of adsorption, %				
	5 min	10 min	30 min	90 min	Day
Zn(II)	86.60	86.60	86.60	86.60	99.84
Pb(II)	33.10	33.10	33.10	33.10	65.53
Cu(II)	65.32	67.54	67.54	70.53	83.50
Cd(II)	93.06	93.51	93.51	94.11	94.11
Fe(III)	100.00	100.00	100.00	100.00	72.01
V(V)	99.93	99.93	99.93	99.93	99.94
Mo(VI)	96.08	97.61	98.04	98.26	99.93

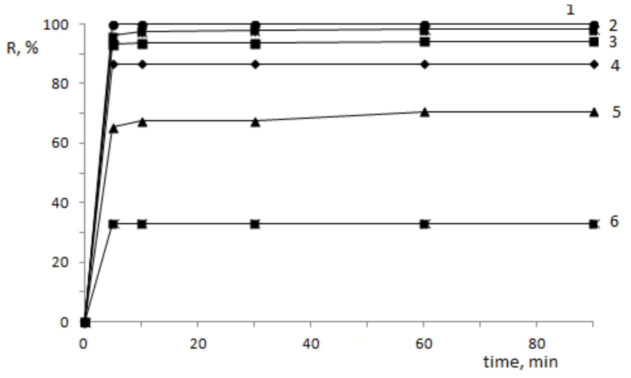


Fig. 7. Dependence of degree of adsorption (*R*, %) on time of contact with solutions containing 100 μg of iron in distilled water and 200 μg of vanadium at pH 5.1 (1), 200 μg of molybdenum in distilled water (2), 500 μg of cadmium at pH 2.5 (3), 500 μg of zinc at pH 8.0 (4), 100 μg of copper at pH 8.0, (5) and 100 μg of lead at pH 2.5 (6)

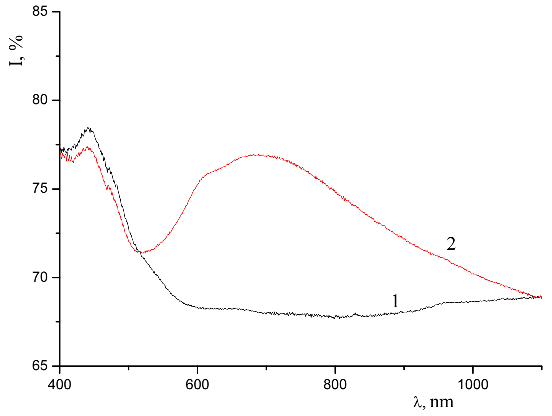


Fig. 8. DRES of silica-chitosan composite with adsorbed 50 μg (1) and 700 μg of copper (2)

The DRESs with different amount of adsorbed lead (Fig. 10) have the band of interligand transitions of chitosan with the maximum at 450 nm, the band of charge transition ligand-metal at 610 nm and the band of *d–d* transitions of lead at 910 nm.

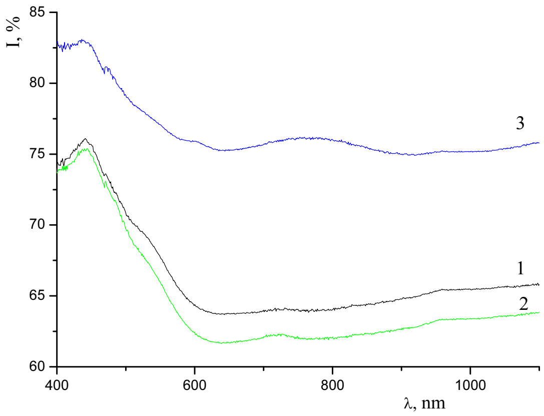


Fig. 9. DRES of composite with the adsorbed 50 µg (1), 400 µg (2) and 1.2 mg of molybdenum (3)

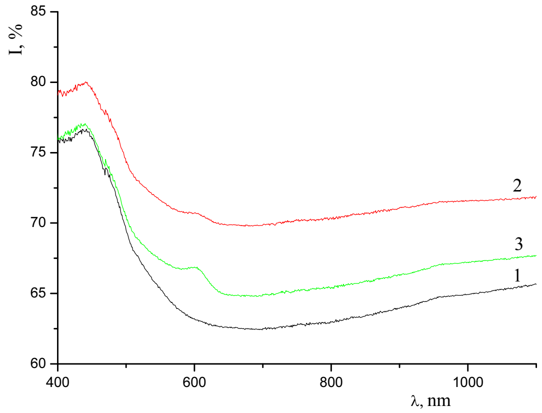


Fig. 10. DRES of composite with the adsorbed 50 µg (1), 200 µg (2) and 500 µg of lead (3)

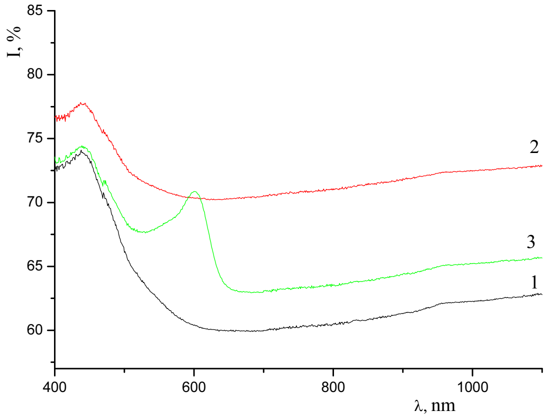


Fig. 11. DRES of silica-chitosan composite with adsorbed 50, 200 and 500 µg of cadmium (1–3 respectively)

Bands of interligand transitions of chitosan with the maximum at 450 nm and band of *d* – *d* transition of metal with maximum at 960 nm were observed in the DRES of composite with adsorbed Cd(II) ions (Fig. 11). The band of charge transition ligand-metal at 610 nm is present only in the spectrum of the composite, which adsorbed 200 µg of metal.

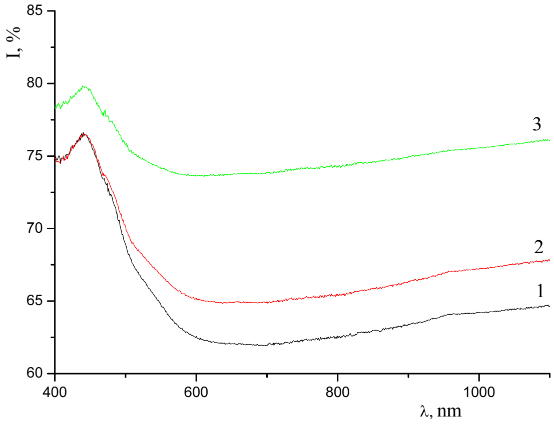


Fig. 12. DRES of silica-chitosan composite with 50, 200 and 500 µg of zinc (1–3 respectively)

For the electronic spectra of composite with adsorbed zinc ions, only bands of interligand transitions of chitosan with maximum at 450 nm and the band of *d* – *d* metal transitions with maximum at 960 nm were detected, but the band of charge transition ligand-metal is absent (Fig. 12).

4. CONCLUSIONS

The composite silica-chitosan was synthesized by crosslinking of adsorbed biopolymer with glutaraldehyde. IR spectroscopy confirmed the fact of immobilization of chitosan in the surface layer of silica. According to the thermogravimetric analysis the obtained composite contains up to 10 % of chitosan.

The silica with immobilized chitosan on its surface showed adsorption activity towards microquantities of Zn(II), Cd(II), Pb(II), Cu(II), Fe(III), Mo(VI) and V(V) ions in the aqueous medium. It was shown that the kinetic characteristics of the synthesized composite with respect to studied ions are similar to that for inorganic adsorbents.

The synthesized composite was found to show adsorption activity with respect to milligram amounts of toxic metal ions. In particular, it removes quantitatively Zn(II), V(V) and Mo(VI) ions (up to 0.46, 0.31 and 0.02 mmol/g, respectively) and 30 % – 80 % of the Cu(II) ions in pH range from 1.0 to 8.0. At pH 2.5 – 7.0 the obtained adsorbent extracts from 56 % up to 67 % Pb(II) ions and 65 % Cd(II) ions at pH 2.5 from a solution composed of acetate ions. It was shown that the maximum adsorption capacity of silica with immobilized chitosan with respect to all studied ions is achieved within a few minutes of contact with the solution.

REFERENCES

1. **Singhon, R., Husson, J., Knorr, M., Euvrard, M.** Preparation of Silica-Supported Biosorbents for Copper(II) Removal *Journal of Dispersion Science and Technology* 32 (12) 2011: pp. 1735 – 1741. http://dx.doi.org/10.1080/01932691.2011.616133
2. **Repo, E., Warchoł, J. K., Bhatnagar, A., Sillanpää, M.** Heavy Metals Adsorption by Novel EDTA-modified Chitosan–Silica Hybrid Materials *Journal of Colloid and Interface Science* 358 (1) 2011: pp. 261 – 267. http://dx.doi.org/10.1016/j.jcis.2011.02.059

3. **Gandhi, M. R., Meenakshi, S.** Preparation and Characterization of Silica Gel/Chitosan Composite for the Removal of Cu(II) and Pb(II) *International Journal of Biological Macromolecules* 50 (3) 2012: pp. 650 – 657. http://dx.doi.org/10.1016/j.ijbiomac.2012.01.012
4. **He, J.-C., Zhou, F.-Q., Mao, Y.-F., Tanga, Z.-N., Li,C.-Y.** Preconcentration of Trace Cadmium(II) and Copper(II) in Environmental Water Using a Column Packed with Modified Silica Gel-Chitosan Prior to Flame Atomic Absorption Spectrometry Determination *Analytical Letters* 46 (9) 2013: pp. 1430 – 1441.
5. **Kalyani, S., Ajitha Priya, J., Srinivasa Rao, P., Krishnaiah, A.** Removal of Copper and Nickel from Aqueous Solutions Using Chitosan Coated on Perlite as Biosorbent *Separation Science and Technology* 40 (7) 2005: pp. 1483 – 1495.
6. **Kalyani, S., Krishnaiah, A., Boddu, V. M.** Adsorption of Divalent Cobalt from Aqueous Solution onto Chitosan-coated Perlite Beads as Biosorbent *Separation Science and Technology* 42 (12) 2007: pp. 2767 – 2786.
7. **Copello, G. J., Varela, F., Martínez Vivot, R., Díaz, L. E.** Immobilized Chitosan as Biosorbent for the Removal of Cd(II), Cr(III) and Cr(VI) from Aqueous Solutions *Bioresource Technology* 99 (14) 2008: pp. 6538 – 6544.
8. **Dragan, E. S., Dinu, M. V.** Removal of Copper Ions from Aqueous Solution by Adsorption on Ionic Hybrids Based on Chitosan and Clinoptilolite *Ion Exchange Letters* 2 2009: pp. 15 – 18.
9. **Zou, X., Pan, J., Ou, H., Wang, X., Guan, W., Li, C., Yan, Y., Duan, Y.** Adsorptive Removal of Cr(III) and Fe(III) from Aqueous Solution by Chitosan/Attapulgite Composites: Equilibrium, Thermodynamics and Kinetics *Chemical Engineering Journal* 167 (1) 2011: pp.112 – 121.
10. **Gupta, N., Kushwaha, A. K., Chattopadhyaya, M. C.** Adsorptive Removal of Pb^{2+}, Co^{2+} and Ni^{2+} by Hydroxyapatite/Chitosan Composite from Aqueous Solution *Journal of the Taiwan Institute of Chemical Engineers* 43 (1) 2012: pp. 125 – 131.
11. **Tirtom, V. N., Dinçer, A., Becerik, S., Aydemir, T., Çelik, A.** Comparative Adsorption of Ni(II) and Cd(II) Ions on Epichlorohydrin Crosslinked Chitosan–Clay Composite Beads in Aqueous Solution *Chemical Engineering Journal* 197 2012: pp. 379 – 386.
12. **Tirtom, V. N., Dinçer, A., Becerik, S., Aydemir, T., Çelik, A.** Removal of Lead(II) Ions from Aqueous Solution by Using Crosslinked Chitosan-Clay Beads *Desalination Water Treatment* 39 (1 – 3) 2012: pp. 76 – 82.
13. **Varma, A. J., Deshpandea, S. V., Kennedy, J. F.** Metal Complexation by Chitosan and its Derivatives: a Review *Carbohydrate Polymers* 55 2004: pp. 77 – 93.
14. **Kolodynska, D.** Chitosan as an Effective Low-cost Sorbent of Heavy Metal Complexes with the Polyasparic Acid *Chemical Engineering Journal,* 173 2011: pp. 520 – 529.
15. **Kolodynska, D.** Adsorption Characteristics of Chitosan Modified by Chelating Agents of a New Generation *Chemical Engineering Journal* 179 2012: pp. 33 – 43.
16. **Korostyliov, P. P.** Solution Preparation for Chemical-Analytical Application. Moscow, Science, 1964: 399 p. (in Russian).
17. **Marchenko, Z., Balcerzak, M.** Spectrofotometry Metods in Inorganic Analisys. Warsaw, Naukove, Naukowe PWN, 1998 (in Polish).
18. **Schebrov, D. P., Matveets, M. A.** Analytical Chemistry of Cadmium. Moscow, Science, 1973: 256 p. (in Russian).
19. **Muzgin,, V. N., Halezina, V. L., Zolotavin, V. L., Bezrukov, I. Ya.** Analytical Chemistry of Vanadium. Moscow, Science, 1981: 215 p. (in Russian).
20. **Kulyk, T. V., Palyanytsya, B. B., Borodavka, T. V., Borysenko, M. V.** Supramolecular Structures of Chitosan on the Surface of Fumed Silica. In book: Nanomaterials and Supramolecular Structures. Shpak A. P., Gorbyk P. P. (eds.). Springer Science Business Media B.V., 2009: pp. 259 – 268. http://dx.doi.org/10.1007/978-90-481-2309-4_21