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CHITOSAN IMMOBILIZED ON SAPONITE SURFACE IN EXTRACTION OF V(V), Mo(VI) AND Cr(VI) OXOANIONS

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Chitosan-saponite composite has been obtained by crosslinking of adsorbed on saponite surface biopolymer with glutaraldehyde. The structure of composite was studied by IR-spectroscopy, concentration of immobilized chitosan was estimated using thermogravimetric analysis. The adsorption of microquantities of V(V), Mo(VI), and Cr(VI) oxoanions by obtained composite, initial natural mineral and polymer has been studied from aqueous solutions. The sorption capacities and kinetics adsorption characteristics of the composite adsorbent were estimated.

Keywords: adsorption, chitosan, saponite, clay, vanadium, molybdenum, chromium

INTRODUCTION

Saponite (saponite clay) of Ukrainian Podillya refers to the class of bentonites, subclass of layered magnesium silicate montmorillonite where Al³⁺ are almost completely replaced by Mg²⁺ and Si⁴⁺ replaced by Al³⁺ in their structural framework. Besides of those elements, the structure of saponite includes more than 35 other biological active chemical elements in micro and ultramicro amounts: iron, fluorine, calcium, potassium, sodium, zinc, cobalt, copper, nickel, vanadium, molybdenum, *etc.* According to the fact that the natural mineral possesses ion-exchanging and adsorption properties, it is widely used in treatment technologies as mineral fertilizer, food additive in animal husbandry and cosmetics. In Ukraine saponite was certificated as lightly porous filler; as sorbent for milk, milk products and other liquid food products purification from heavy metals and radionuclides; as complex mineral additive for fodders [1–5].

Adsorbents of natural origin are widely used for water treatment in order to replace current costly methods of heavy metals elimination from solutions. To improve the adsorption properties of mineral adsorbents it is expedient to immobilize the appropriate substances with well-pronounced ion-exchanging and complexing properties onto their surfaces. Application for these purpose natural biopolymers, such as a nitrogen-containing polysaccharide chitosan, is of a great interest [6–8].

Properties of inorganic sorbents could be upgraded by valuable characteristics of organic polymer. In particular, chitosan has good biocompatibility, high adhesion to the surface, a wide range of pH stability, expressed chelating properties. Natural minerals are characterized by advanced surface stability in the acidic medium, acceptable kinetics, thermal stability, and resistance to microbial attack.

Recent studies in that field have been shown that composites of silica and chitosan [6–13] and biosorbents based on chitosan and different natural minerals [14–21] can be used for extraction and concentration of toxic metals from solutions. However, there is necessity in systematic investigations of adsorption properties of chitosan-mineral composites, in particular to study an effect of nature and pH of solutions and to determine achievable values of adsorption capacity. The peculiarities of chitosan coating formation on the surface of saponite, as well as adsorption properties of the synthesized composite with respect to vanadium(V), molybdenum(VI), and chromium(VI) oxoanions have been studied in this work.

EXPERIMENTAL SECTION

Saponite of Ukrainian Podillya with general formula (Ca₅,Na)₃(Mg,Fe)₃(Si,Al)₄O₁₀(OH)₂·4H₂O was impregnated by chitosan solution (Sigma Aldrich, N 417 963) with a molecular weight from 190,000 to 370,000 Da, degree of deacetylation – not less than 75 % and solubility 10 mg/ml. 20 g of

saponite and 285 ml of 7 mg/ml chitosan solution in acetic acid (pH 2.6) were put in flat-bottom flask and mixed by the magnetic stirrer MM-5 for 2 h. The obtained substance was dried at 50 °C. The structure of surface of saponite with adsorbed chitosan is schematically presented in Fig. 1.

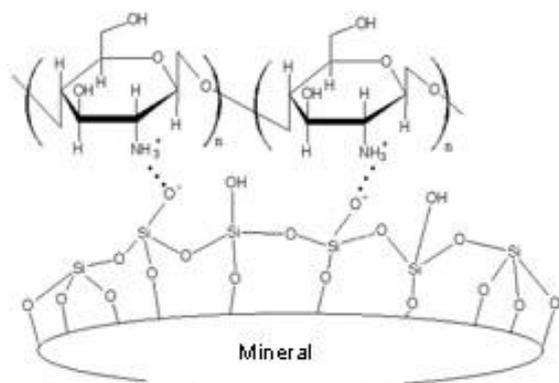


Fig. 1. The scheme of interaction between saponite surface and adsorbed chitosan

Crosslinking of adsorbed polymer with glutaraldehyde was performed in order to consolidate better the surface layer because it is important in case of application of the composite in the acidic solutions. For this purpose, 10 ml of 0.025 % glutaraldehyde solution was added to the saponite with the preadsorbed chitosan and stirred for 2 h. According to the calculations, used amount of dialdehyde provides crosslinking about 5 % of amino groups in the polymer layer. The obtained product was washed with repeated decantation and dried at 50 °C to constant weight. As a result, chitosan-saponite composite with weight ratio chitosan: silica – 1:10 was synthesized.

The investigations of adsorption properties of the obtained composite with respect to V(V), Mo(VI), and Cr(VI) oxoanions were carried out in the static mode with periodic hand-stirring. For that, sample of 0.1 g of synthesized adsorbent was contacted with 25 ml of solutions with different concentrations of salts: NH_4VO_3 , $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ prepared under recommendations [22]. Photometric studies of equilibrium solutions were performed according to the methods described in [23, 24] 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 saponite was determined by thermogravimetric method on a Q-1500 MOM (Hungary) derivatograph with the computer data registration in the temperature range 15–1000 °C. Samples heating rate was 10 degrees/min. DTA, TG and DTG curves were recorded simultaneously.

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

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

where m_0 is the weight of the metal in the initial solution, m_{ads} is the weight of adsorbed metal, m is the weight 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.

RESULTS AND DISCUSSION

In the FTIR spectrum of chitosan (Fig. 2) the band at 3429 cm^{-1} corresponds to the stretching vibrations O–H of hydroxyl groups bound with carbon atoms. Intensive absorbance bands at $2800\text{--}3000 \text{ cm}^{-1}$ due to the C–H stretching vibrations. The bands 1580 cm^{-1} of the bending vibrations of $-\text{NH}_2$, 1420 and 1380 cm^{-1} for C–H bending vibrations, 1310 cm^{-1} for asymmetric C–O–C stretching vibrations, and 1080 cm^{-1} for C–O stretching vibration of CH–OH were observed.

The FTIR spectrum of the synthesized chitosan-saponite has shown a shift of the band of $-\text{NH}_2$ bending vibrations in comparison with the spectrum of initial chitosan. An intensive absorbance at 1000 cm^{-1} represents the Si–O stretching vibrations. The bands at 518 and 466 cm^{-1} correspond to Al–O–Si and Si–O–Si bending vibrations, respectively. FTIR spectrum of composite showed the absorption band at 1650 cm^{-1} which corresponds to stretching vibrations of azomethine bonds C=N formed after treatment with glutaraldehyde [25, 26].

The thermogravimetric analysis (hereinafter – TG) of saponite, chitosan and synthesized composite were conducted in order to determine the concentration of immobilized chitosan (Fig. 3). For TG-curve of chitosan (Fig. 3 a) two decomposition temperature can be noticed. The initial weight loss of 11 % from room temperature (30 °C) up to 190 °C corresponds to the release of adsorbed water. The second recorded

decomposition region (190–1000 °C) completely applies to weight loss of chitosan. As for clay (рис. 3 *b*), the first decomposition (30–200 °C) corresponds to the weight loss of 11 % due to removal of adsorbed water. The next weight loss (200–1000 °C) involved major weight loss of the hydroxyl structure in clay, with 83 % residue remained as metal oxides included into the

composition of the mineral. The thermogravimetric curve of composite chitosan-saponite (Fig. 3 *c*) is characterized by decomposition region from 30 to 200 °C which is similar to initial materials and corresponds to water desorption with following decomposition of organic part of composite at higher temperatures (200–1000 °C). Similar observations have been found in [25, 28–30].

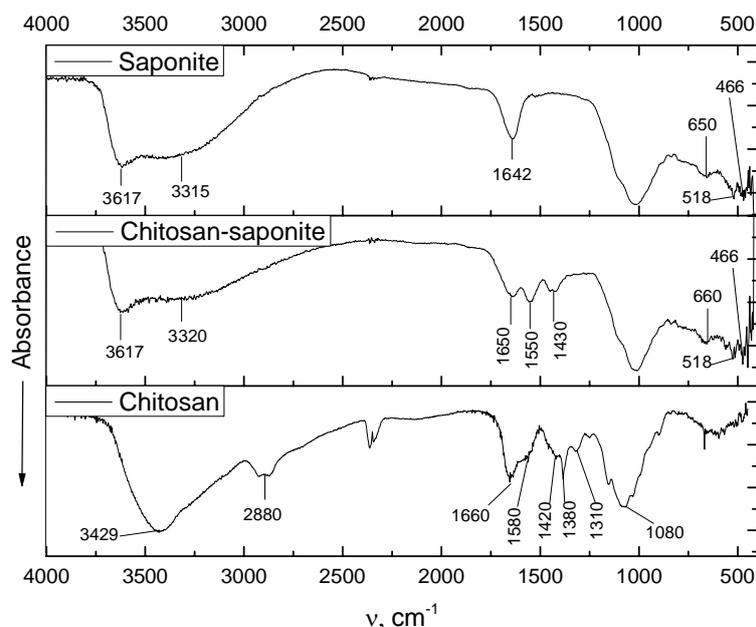


Fig. 2. FTIR spectra of saponite, chitosan and composite chitosan-saponite

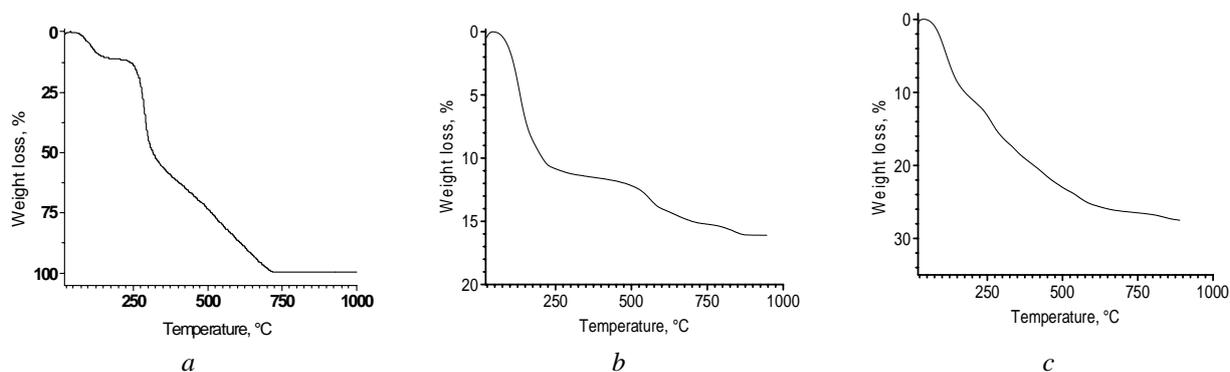


Fig. 3. TG-curves of chitosan (*a*), saponite (*b*) and composite chitosan-saponite (*c*)

The comparison of TG-curves of saponite, chitosan and composite chitosan-saponite shows that in the temperature range from 200 to 1000 °C weight losses of the composite silica-chitosan, which are most likely caused by destruction of the organic component of the composite, reach about 9.1 %. Comparison this value with the weight of chitosan, which has been taken for the composite synthesis, shows almost complete polymer

anchorage on the saponite surface. According to that, one gram of the carrier was coated by approximately 91 mg of chitosan.

First of all, at investigation of sorption properties of the synthesized composite optimum values of medium acidity for the highest removal of the studied ions were determined. It can be seen from Fig. 4 that 300 mg of vanadium are quantitatively adsorbed by surface of synthesized

composite in pH range from 1 to 8. The high adsorption capacities of synthesized composite with respect of hexavalent molybdenum and chromium oxoions were observed at pH 2.5 and in the neutral medium. However, the quantitative adsorption was not detected in all range of acidity of the medium. The maximum degree of sorption (from solution containing 1 mg of molybdenum) by synthesized composite was about 92 % in the acidic medium (pH 2.5) created with acetate ions.

As it can be seen from Fig. 4, 66 and 68 % of molybdenum(VI) oxoanions were extracted from the slightly acidic medium at pH 5.0 and from distilled water, respectively. In the strongly acidic medium (pH 1.0, 0.1 M HCl) the degree of adsorption of those oxoanions was 46 % (Table 1). The lowest degree of adsorption (40 %) of molybdate-ions MoO_4^{2-} has been observed in the slightly alkaline medium at pH 8.0 generated by the ammonium acetate buffer. From solution containing 100 μg of chromium, oxoions Cr(VI) were higher (75–86 %) concentrated by the synthesized composite in pH range from 2.5 to 5.0 in the presence of acetate ions and from the neutral

medium. Similarly to molybdenum(VI), in the slightly alkaline medium at pH 8.0 the adsorption of chromium(VI) is decreased (68 %). However, the lowest adsorption of chromate-ions (64 %) was detected in the strongly acidic medium (pH 1.0, in the presence of chloride-ions).

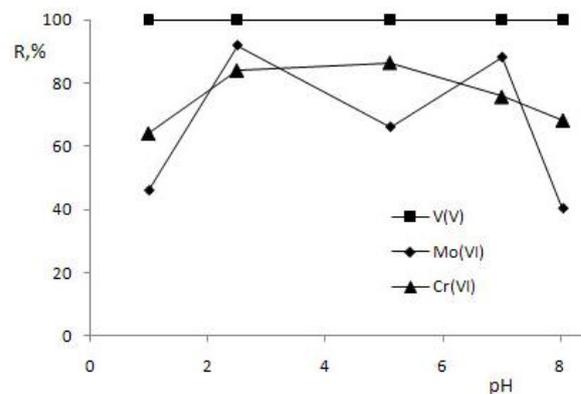


Fig. 4. The degree of adsorption of V(V), Mo(VI), and Cr(VI) oxoanions by composite chitosan-saponite as a function of the medium acidity

Table 1. The degree of adsorption of V(V), Mo(VI), and Cr(VI) oxoanions as a function of the medium acidity (experimental conditions: weight of sorbent – 0.1 g, volume of solution – 25 ml, content of chromium in the initial solution – 0.1 mg, vanadium – 0.3 mg, molybdenum – 1.0 mg)

| Oxoanions | Degree of adsorption, % | | | | |
|-----------|-------------------------|------------------------------------|------------------------------------|-----------------|--------------------------------------|
| | pH 1.0 HCl | pH 2.5 CH_3COOH | pH 5.0 CH_3COOH | Distilled water | pH 8.0 ammonium acetate buffer |
| V(V) | 99.94 | 99.95 | 99.97 | 99.97 | 99.97 |
| Mo(VI) | 46.12 | 91.87 | 66.13 | 88.10 | 40.48 |
| Cr(VI) | 64.16 | 84.01 | 86.45 | 75.68 | 68.29 |

Thus, the synthesized composite showed adsorption activity with respect to the investigated ions in the different pH ranges. The values of medium acidity, at which the maximum adsorption activities of chitosan-saponite composite for each of studied oxoanions were achieved, correspond to published data of complexation conditions of these ions with amino groups of chitosan in solutions [6–9].

Adsorption isotherms in the static mode for each ion were obtained for calculation of the values of the adsorption capacity of the composite. As it is shown in Fig. 5, the sorption activity of mineral with respect to quinquevalent vanadium oxoanions was increased in the presence of chitosan coating on the carrier surface. In the neutral medium one gram of synthesized composite extracts 0.51 mmol

of vanadate-ions VO_3^- , and the isotherm of adsorption has the stair-step form (Fig. 5, curve 1). Under the same conditions, the initial saponite removes vanadium(V) oxoanions with the maximum capacity 0.33 mmol/g, but the isotherm of adsorption has concave form which confirms that vanadate-ions have low affinity to the saponite surface (Fig. 5, curve 2).

As shown in Fig. 6, from neutral solutions containing from 250 μg to 10 mg of metal the chitosan-saponite composite concentrates molybdate-ions MoO_4^{2-} with maximum adsorption capacity 0.4 mmol/g. In the acidic medium at pH 2.5 the composite removes mixture of MoO_4^{2-} , $[\text{Mo}_6\text{O}_{21}]^{6-}$, $[\text{Mo}_7\text{O}_{24}]^{6-}$ oxoanions with maximum adsorption capacity 0.73 mmol/g. In the similar conditions, initial saponite adsorbs Mo(VI)

oxoanions with maximum capacity 0.22 mmol/g but initially (content of metal from 0.25 to 2.50 mg) the isotherm of adsorption has concaved form which confirms that molybdate-ions have lower affinity to the saponite surface in comparison with that to the surface of organo-mineral composite. The character of isotherms confirms the monolayered distribution of mixture of polymolybdate-ions on the surface as a result of complexation or formation of ionic associates with protonated amino groups of immobilized polymer at pH 2.5 (Fig. 6, curve 1), as well as in the neutral medium (Fig. 6, curve 2).

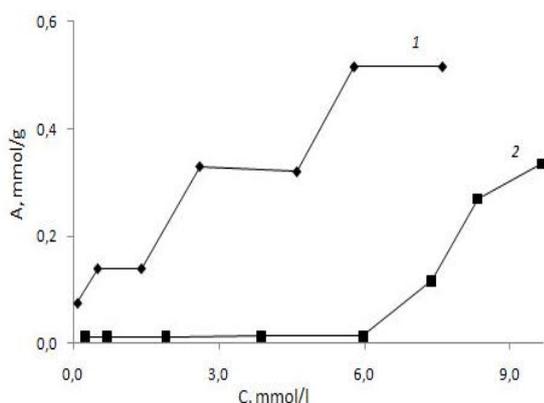


Fig. 5. Adsorption isotherms of V(V) oxoanions by chitosan-saponite composite (1) and initial saponite (2) in the neutral medium

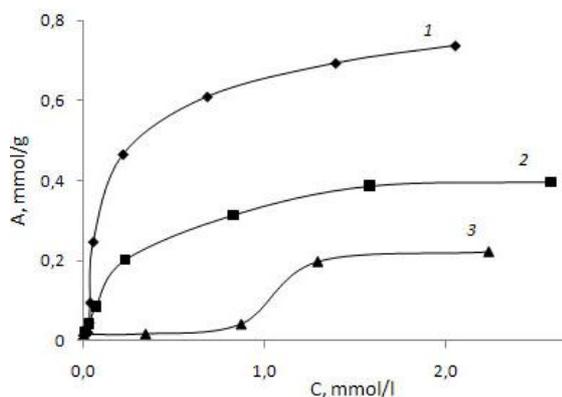


Fig. 6. Adsorption isotherms of Mo(VI) oxoanions by chitosan-saponite composite at pH 2.5 (1) and from distilled water (2), and by initial saponite at pH 2.5 (3)

Initial saponite does not adsorb dichromate-ions, whilst the composite chitosan-saponite has shown high adsorption capacity with respect to these anions (Fig. 7). Adsorption capacity of synthesized composite with respect of Cr(VI) oxoanions is 0.59 mmol/g.

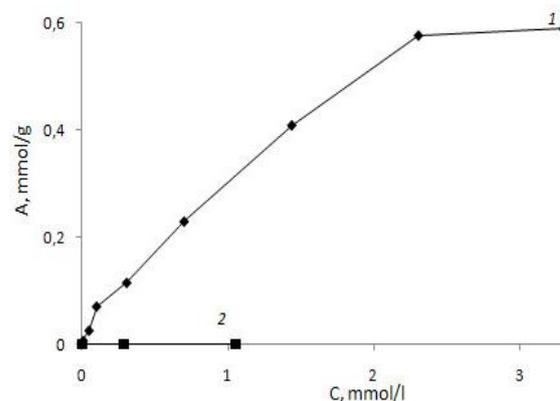


Fig. 7. Adsorption isotherms of Cr(VI) oxoanions by chitosan-saponite composite (1) and initial saponite at pH 5.0 (2)

Obtained values of the adsorption capacities of the composite chitosan-saponite and initial saponite, as well as maximum degrees of adsorption of V(V), Mo(VI), Cr(VI) oxoanions from solutions with different concentrations of metals are shown in Table 2.

Taking into account that there are 9.1 % of chitosan and 90.9 % of mineral in the composite, we have estimated the contribution of organic and inorganic part to the maximum adsorption capacity (A_{\max}) with respect to each of studied ions (Fig. 8). A_{\max} of crosslinked chitosan (5 % of aminogroups were crosslinked by glutaraldehyde) with respect of V(V) oxoanions with initial mass of vanadium 7.5 mg in the neutral medium is 0.09 mmol/g, saponite – 0.11 mmol/g. Under the same conditions, A_{\max} for composite chitosan-saponite is 0.52 mmol/g, which is 2.5 times higher than sum of maximum adsorption capacities of the starting components.

In the acidic medium generated by acetic-ions (pH 2.5), crosslinked chitosan adsorbs Mo(VI) oxoanions with A_{\max} 0.07 mmol/g, saponite – 0.38 mmol/g, but in the same conditions the synthesized composite extracts almost 2.5 times more than initial compounds (A_{\max} runs up to 0.63 mmol/g). It is interesting that the synthesized composite adsorbs chromium(VI) at pH 5.0 with adsorption capacity 0.15 mmol/g which is 5 times higher than capacity of partly crosslinked chitosan under the same experimental conditions: one gram of crosslinked chitosan concentrates 0.02–0.03 mmol/g Cr(VI) oxoanions from the acidic (pH 2.5) and neutral media. Saponite does not show adsorption activity with respect to dichromate-ions $\text{Cr}_2\text{O}_7^{2-}$ at pH 5.0 (acetate buffer).

Table 2. Adsorption capacity of chitosan-saponite composite and initial saponite and maximum degree of adsorption of V(V), Mo(VI), Cr(VI) oxoanions from solutions with various metal concentrations

| Oxoanion | Mo(VI) | Cr(VI) | V(V) | Mo(VI) |
|------------------------------------|-----------------------------|----------------------------|----------------------------|----------------------------|
| pH | 2.5 | 5.0 | Distilled water | |
| <i>Composite chitosan-saponite</i> | | | | |
| adsorption capacity, mmol/g | 0.73 | 0.59 | 0.52 | 0.40 |
| maximum degree of adsorption, % | 94.5 ($m_0=2.5$ mg)* | 86 ($m_0=100$ μ g) | 89 ($m_0=1$ mg) | 90 ($m_0=250$ μ g) |
| <i>Saponite</i> | | | | |
| adsorption capacity, mmol/g | 0.22 | 0 | 0.33 | – |
| maximum degree of adsorption, % | 100 ($m_0=250$ μ g) | – | 36 ($m_0=500$ μ g) | – |

* m_0 – initial content of metal in the solution

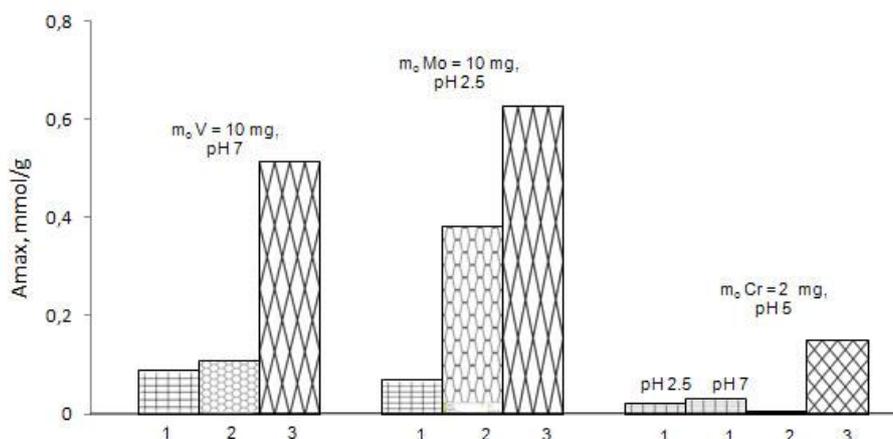


Fig. 8. Comparison (according to mass ratios in the composite) of adsorption capacity of chitosan (1), saponite (2), and composite chitosan-saponite (3) with respect to V(V), Mo(VI), and Cr(VI) oxoanions

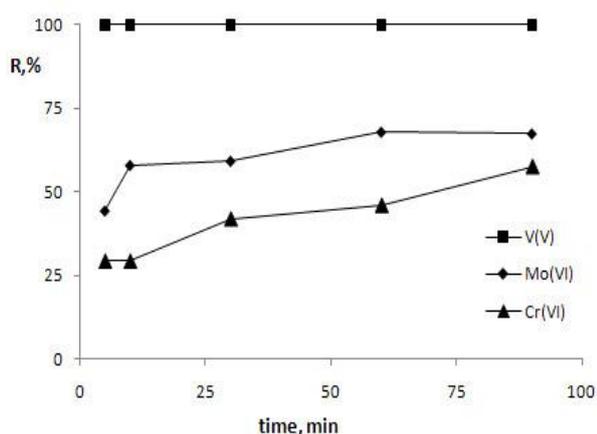


Fig. 9. Dependence of degree of adsorption (R , %) on time of contact with solutions containing 300 μ g of vanadium in distilled water, 1000 μ g of molybdenum at pH 2.5, and 100 μ g of chromium at pH 5.0

According to obtained results for all studied ions (Fig. 9), the degree of adsorption consistently increases during several hours, which is typical for polymeric adsorbents where the sorption characteristics are defined by interaction between ions and functional groups of supported chitosan.

CONCLUSION

The composite chitosan-saponite 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 9.1 % of chitosan.

Saponite with immobilized chitosan on its surface showed better adsorption properties towards microquantities of vanadium, molybdenum, chromium in aqueous solutions in comparison with unmodified mineral. Adsorption

capacity of the synthesized composite with respect to: vanadium(V) – 0.52 mmol/g in the neutral medium; molybdenum(VI) – 0.73 and 0.40 mmol/g at pH 2.5 and in distilled water, respectively; chromium(VI) – 0.59 mmol/g at pH 5.0. Unmodified mineral removes vanadium(V) oxoanions with maximum adsorption capacity 0.33 mmol/g, molybdenum(VI) oxoanions – 0.22 mmol/g at pH 2.5 and does not show adsorption activity with respect to chromium(VI) at pH 5.0. It was shown that the synthesized composite extracted studied metals for the day.

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Імобілізований на поверхні подільського сапоніту хітозан в процесах екстракції V(V), Mo(VI) та Cr(VI) оксоаніонів

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Композит хітозан-сапоніт одержано шийкою глутаровим альдегідом адсорбованого на поверхні Подільського сапоніту біополімеру. Будову поверхні композит досліджено методом ІЧ-спектро-скопії, а кількість іммобілізованого хітозану визначено за допомогою термогравіметричного аналізу. Проведено оцінку адсорбційних характеристик синтезованого композит щодо мікрокількостей V(V), Mo(VI) і Cr(VI) оксоаніонів у водних розчинах у порівнянні з властивостями вихідних природного мінералу і полімеру. Визначено сорбційну ємність та кінетичні характеристики одержаного композитного адсорбенту.

Ключові слова: адсорбція, хітозан, сапоніт, глина, ванадій, молібден, хром

Иммобилизованный на поверхности подольского сапонита хитозан в процессах экстракции V(V), Mo(VI) и Cr(VI) оксоанионов

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Композит хитозан-сапонит получен шийкой адсорбированого на поверхности Подольского сапонита биополімера глутаровым альдегидом. Структура поверхности композита изучена методом ИК-спектроскопии, а концентрация иммобилизованого хитозана установлена из данных термогравиметрического анализа. Проведена оценка адсорбционных характеристик синтезованого

композита по отношению к микроколичествам оксоанионов V(V), Mo(VI) и Cr(VI) в водных растворах в сравнении со свойствами исходных природного минерала и полимера. Установлена сорбционная емкость и кинетические характеристики полученного композитного адсорбента.

Ключевые слова: адсорбция, хитозан, сапонит, глина, ванадий, молибден, хром

REFERENCES

1. Chekman I.S., Ovrutskiy V.I., Shumeyko V.M. et al. Clay as a drug, *Pharm. J.*, 1 (1991) 22 (in Ukrainian).
2. Gyrin V.M., Boiko I.I., Rudichenko V.F. Application of natural mineral saponite for water disinfection, *Likarska sprava*, 5–6 (1995) 177 (in Ukrainian).
3. Chelyshev N.F., Volodin V.F., Kryukov V.L. Ion-exchanging Properties of Natural Zeolites, Moscow, Science, 1988, 129 p. (in Russian).
4. Tsitsishvili G.V., Andronikashvili T.G., Kirov G.N., Filizova L.D. Natural Zeolites, Moscow, Chemistry, 1985, 224 p. (in Russian).
5. Tarasevich Yu.I. Natural Sorbents for Water Purification, Kyiv, Naukova dumka, 1981, 207 p. (in Ukrainian).
6. Budnyak T.M., Tertykh V.A., Yanovska E.S. Chitosan and its derivatives as sorbents for effective removal of metal ions, *Surface*, 5(20) (2013) 118 (in Ukrainian).
7. Varma A.J., Deshpande S.V., Kennedy J.F. Metal complexation by chitosan and its derivatives: a review, *Carbohydr. Polym.*, 55 (2004) 77.
8. Grini G. Recent development in polysaccharide-based materials used as adsorbents in wastewater treatment, *Prog. Polym. Sci.*, 30 (2005) 38.
9. Singhon R., Husson J., Knorr M., Euvrard M. Preparation of silica-supported biosorbents for copper(II) removal, *J. Disper. Sci. Technol.*, 32 (2011) 1735.
10. Repo E., Warchol J.K., Bhatnagar A., Sillanpää M. Heavy metals adsorption by novel EDTA-modified chitosan–silica hybrid materials, *J. Colloid Interf. Sci.*, 358 (2011) 261.
11. Gandhi M.R., Meenakshi S. Preparation and characterization of silica gel/chitosan composite for the removal of Cu(II) and Pb(II), *Int. J. Biol. Macromol.*, 50 (2012) 650.
12. He J.-C., Zhou F.-Q., Mao Y.-F. et al. 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 (2013) 1430.
13. Copello G.J., Varela F., Vivot R.M., Díaz L.E. Immobilized chitosan as biosorbent for the removal of Cd(II), Cr(III) and Cr(VI) from aqueous solutions, *Bioresource Technol.*, 99 (2008) 6538.
14. Wan Ngah W.S., Teong L.C., Hanafiah M.A.K.M. Adsorption of dyes and heavy metal ions by chitosan composites: A review, *Carbohydr. Polym.*, 83 (2011) 1446.
15. Kalyani S., Priya J.A., Rao P.S., Krishnaiah A. Removal of copper and nickel from aqueous solutions using chitosan coated on perlite as biosorbent, *Separ. Sci. Technol.*, 40 (2005) 1483.
16. Kalyani S., Krishnaiah A., Boddu V.M. Adsorption of divalent cobalt from aqueous solution onto chitosan-coated perlite beads as biosorbent, *Separ. Sci. Technol.*, 42 (2007) 2767.
17. 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) 15.
18. Zou X., Pan J., Ou H. et al. Adsorptive removal of Cr(III) and Fe(III) from aqueous solution by chitosan/attapulgite composites: Equilibrium, thermodynamics and kinetics, *Chem. Eng. J.*, 167 (2011) 112.
19. Gupta N., Kushwaha A.K., Chattopadhyaya M.C. Adsorptive removal of Pb²⁺, Co²⁺ and Ni²⁺ by hydroxyapatite/chitosan composite from aqueous solution, *J. Taiwan Inst. Chem. E*, 43 (2012) 125.
20. Tirtom V.N., Dinçer A., Becerik S. et al. Comparative adsorption of Ni(II) and Cd(II) ions on epichlorohydrin crosslinked chitosan–clay composite beads in aqueous solution, *Chem. Eng. J.*, 197 (2012) 379.
21. Tirtom V.N., Dinçer A., Becerik S. et al. Removal of lead(II) ions from aqueous solution by using crosslinked chitosan-clay beads, *Desalination and Water Treatment*, 39 (2012) 76.
22. Korostyliov P.P. Solution Preparation for Chemical-Analytical Application, Moscow, Science, 1964, 399 p. (in Russian).

23. Marchenko Z., Balcerzak M. Spectrofotometry Methods in Inorganic Analysis, Warsaw, Naukowe, Naukowe PWN, 1998 (in Polish).
24. Muzgin V.N., Halezina V.L., Zolotavin V.L., Bezrukov I.Ya. Analytical Chemistry of Vanadium, Moscow, Science, 1981, 215 p. (in Russian).
25. Wan Ngah W.S., Teong L.C., Wong C.S., Hanafiah M.A.K.M. Preparation and characterization of chitosan-zeolite composites, *J. Appl. Polym. Sci.*, 125 (2012) 2417.
26. Perminov P.A. Patterns of interaction of chitosan with glutaraldehyde and their use in the preparation of enzyme-polymer materials: Ph.D (speciality 02.00.06) Thesis Abstract, A.N. Kosygin MSU, Moscow, 2010, 16 p. (in Russian).
27. Guibal E., Milot C., Tobin J. Metal-anion sorption by chitosan beads: equilibrium and kinetic studies, *Ind. Eng. Chem. Res.*, 37 (1998) 1454.
28. Futralan C. M., Kan C. C., Dalida M. L. et al. Fixed-bed column studies on the removal of copper using chitosan immobilized on bentonite, *Carbohydr. Polym.*, 83 (2011) 697.
29. Jaworska M., Sakurai K., Gaudon P., Guibal E. Influence of chitosan characteristics on polymer properties. I: Crystallographic properties, *Polym. Int.*, 52 (2003) 198.
30. Yang X., Tu Y., Shang S., Tao X. Well-dispersed chitosan/graphene oxide nanocomposites, *App. Mater. Interfaces*, 2 (2010) 1707.
31. Budnyak T.M., Yanovska E.S., Tertykh V.A., Voznyk V.I. Adsorption properties of composite Sokirnitsky clinoptilolite-polyaniline towards anions of elements V and VI groups of D.I. Mendeleev Periodic System, *Reports of the National Academy of Sciences of Ukraine*, 3 (2011) 141 (in Ukrainian).

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