

Sorption properties of saponite clay, *in situ* modified by poly(4-vinylpyridine-co-styrene), towards Cu(II), Cd(II), Pb(II), Mn(II) and Fe(III) ions.

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In situ modification with copolymer of 4-vinylpyridine and styrene (molar ratio 3:1) of natural mineral saponite from deposit Tashkivske (Ukraine) by radical polymerization was carried out. Anchorage of organic polymer 4-vinylpyridine-co-styrene on the mineral surface was proved by IR spectroscopy, mass spectrometry and scanning electron microscopy. The amount of immobilized copolymer in the synthesized composite material according to the thermogravimetric analysis is 8.5 wt.%. The recorded adsorption capacity of the composite with respect to Cu(II), Pb(II) and Fe(III) ions was increased in comparison with native mineral saponite.

Introduction

Saponite clay (saponite) is a unique natural form of volcanic origin, whose industrial deposits were first discovered in Ukraine. The most promising for solving a number of environmental problems are Tashkivske and Varvarivske deposits of saponite clay in the Khmelnytsky region. Saponite of Tashkivske deposit is certified in Ukraine as light porous filler; as a cleanser of dairy and other liquid food products from salts of heavy metals and radionuclides; as a complex mineral supplement

for feeding livestock and as a biologically active additive [1-3].

In order to improve the sorption properties of natural minerals, it is expedient to modify their surface with multifunctional polymers capable to complexation or ion exchange, e.g. polyionenes, polyhexamethylene guanidine and its derivatives, polyaniline, polyacrylic acid [4-9].

Pyridine and its derivatives are well-known ligands which form strong complexes with most transition metals ions. Processes of

complex formation are also typical for pyridine-containing polymers [10]. Therefore, the modification of the surface of porous inorganic materials by pyridine-based polymers is a perspective approach to produce new composite materials that can be used as effective sorbents of metal cations due to their complexation with Nitrogen atoms of pyridine function in immobilized polymer [11].

One of the promising ways of creating such organo-mineral composite materials with interesting and valuable sorption properties is polymer immobilization *in situ* on the surface of a porous inorganic carrier [12]. The advantage of this method of polymer immobilization is its versatility with respect to the chemical nature of the carrier. The *in situ* method can be successfully applied to carriers of different shapes and rigidity. Moreover, such a method is the only way to obtain a polymer layer on porous and powdered nanoscale carriers [13]. And in the case of immobilization of copolymers it is possible to create a polymeric layer on the surface of an inorganic carrier with the most optimal ratio of copolymer components.

The laws of immobilization and chemical binding of the organic polymers on the surface of mineral carriers with different chemical nature are not fully understood and their research remains relevant.

In [14] we have shown that *in situ* immobilization of copolymer of 4-vinylpyridine

and styrene with molar ratio 4:1 on the silica gel surface allowed us to obtain a material with good sorption activity towards Pb(II), Mn(II), Ni(II) and Fe(III) ions. In our further investigations it was found out that the best sorption capacity to Cu(II), Pb(II) and Fe(III) ions as well as with properties stability in water media exhibited silica gel modified with copolymer 4-vinylpyridine : styrene with molar ratio 3:1.

This work is devoted to *in situ* modification of the natural mineral saponite from Tashkivske deposit by poly(4-vinylpyridine-*co*-styrene) with the molar ratio 3:1 and to the study of the sorption properties of the modified mineral with respect to Cu(II), Cd(II), Pb(II), Mn(II) and Fe(III) ions.

Experimental part

As a mineral porous carrier for the organic complexing polymer, saponite clay from the Tashkivske deposit (Slavutsky district, Khmelnytsky region) was used. The chemical composition as well as physical and chemical properties of saponite is described in [1].

Styrene (Merck) and 4-vinylpyridine (reagent grade, Ukraine) were distilled under vacuum and stored under argon at 3–5 °C. The reagent grade 2,2'-azobis(2-methylpropionitrile) (AIBN, Ukraine) was employed as an initiator of polymerization and other chemicals of p.a. quality (Sigma-Aldrich Inc.) were used as received.

Surface modification of saponite with a copolymer was carried out by heterogeneous copolymerization of 4-vinylpyridine and styrene in CCl_4 in the presence of saponite by the following procedure:

4.82 ml (42 mmol) of styrene, 13.68 ml (127 mmol) of 4-vinylpyridine and 0.185 g of AIBN were dissolved in 73 ml of CCl_4 and poured into a round bottom flask containing 30 g of Saponite. The reaction mixture was further purged with Argon for 30 minutes. The reaction mixture was heated to 75°C for 5 hours at constant stirring. Then the synthesized composite was exposed for 24 hours at room temperature and washed with CCl_4 , filtered off and dried in the air at room temperature for 24 hours.

The scheme of *in situ* immobilization of the obtained complexing copolymer poly(4-vinylpyridine-*co*-styrene) on the saponite surface is shown on Figure 1.

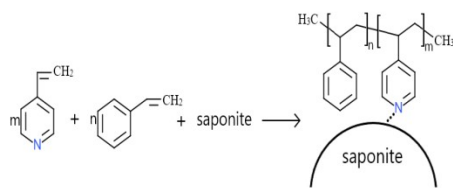


Figure 1. The scheme of *in situ* surface modification of saponite with organic copolymer poly(4-vinylpyridine-*co*-styrene)

FT-IR spectra of parent and modified saponite were recorded on a “Spectrum BX” IR spectrometer with Fourier transformation (Perkin Elmer, Germany) in the spectral range of $500\text{--}4000\text{ cm}^{-1}$ in KBr.

The amount of immobilized copolymer in the obtained composite was evaluated by thermogravimetry using TG / DTA analyzer “Shimadzu DTG-60 H” (Shimadzu, Japan) in the temperature range $15\text{--}1000^\circ\text{C}$. The rate of the samples heating was $10^\circ\text{C min}^{-1}$.

Thermal analysis of the composite was performed on differential scanning calorimeter STA 449 Jupiter F1 (Netzsch, Germany) coupled with a mass spectrometer “QMS 403C” (Germany).

The values of the surface area and the average pore diameter were calculated from the isotherms of low temperature nitrogen adsorption/desorption using the ASAP 2420 V1.01 sorptometer software (Micromeritics, USA). All samples were degassed at 60°C for 24 hours before measurements.

The morphology of the saponite surface before and after modification with poly(4-vinylpyridine-*co*-styrene) was investigated by scanning electron microscopy using the electron microscope “SEM LEO 1430 VP” (Carl Zeiss, Germany).

The sorption characteristics of the synthesized material with respect to the ions Cu(II) , Cd(II) , Pb(II) , Mn(II) and Fe(III) were studied in static mode. The composite (0.1 g) was contacted with 25–100 ml of nitrate working solutions of the corresponding metals. The interaction took place for 10, 20, 40, 60, 120 minutes and 24 hours with constant mechanical shaking. The equilibrium

concentrations of metal ions were measured by the atomic absorption method.

The nitrate working solutions of corresponding metals were prepared from the sets “standard samples of solutions” of the salts (manufactured by A. V. Bogatsky Institute of Physics and Chemistry, Odesa) on the background of 1 M HNO₃ at concentrations of 1 and 10 mg/ml without adding of any buffer solutions.

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

$$R = (m_{ads}/m_o) \cdot 100\% = (m_o - [m])/m_o \cdot 100\% \quad (1),$$

Where m_o - mass of the metal in the output solution, m_{ads} - mass of adsorbed metal, $[m]$ - mass of metal in the equilibrium solution after sorption, which was calculated as $[m] = [M] \cdot V$, where $[M]$ is the equilibrium concentration of the metal and V - volume of equilibrium solution.

The equilibrium concentration of ions of metals was determined by the atomic absorption method. Atomic absorption measurements were carried out using a flame atomic absorption spectrophotometer “Saturn” (Ukraine) in the flame “air - propane - butane” mixture. The wavelengths of the measurements were for Cu - 324.7 nm, Cd - 228.8 nm, Pb - 283.3 nm, Fe - 248.3 nm, and the slit width 0.5 cm. Calculations of equilibrium concentrations in the solution were made by comparing the intensities of their lines in the spectrum with the

intensity of the lines of standard solutions. For this purpose, standard solutions were prepared with metal concentrations in a range 0.1-1.5 µg/ml.

Results and discussion

An immobilization of 4-vinylpyridine-*co*-styrene polymer on the Saponite surface was established by comparison of the initial and modified saponite IR spectra, as shown on Figure 2.

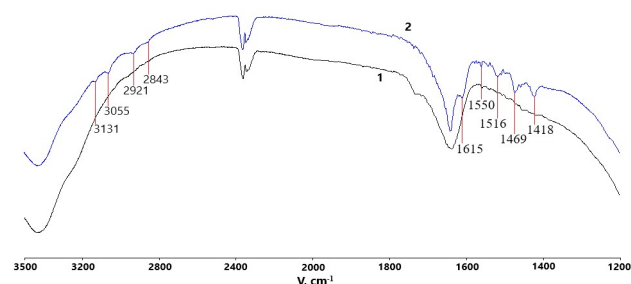


Figure 2. FT-IR spectra of parent saponite (1) and saponite modified with copolymer poly(4-vinylpyridine-*co*-styrene) (2)

As can be seen, in the modified saponite spectrum, the following characteristic absorption bands of the immobilized copolymer are presented:

- bands at 1418, 1469, 1516, 1615 and 1550 cm⁻¹, which can be attributed to the C-N and C=C vibrations in the aromatic systems of styrene and 4-vinylpyridine;
- bands at 2843 and 2921 cm⁻¹ (ν(C-H) of CH and CH₂ groups of the main polymer chain) as well as band at 3055 cm⁻¹ (ν(C-H) vibration in the aromatic moiety) that confirm copolymer formation on the inorganic carrier surface [15].

The amount of immobilized copolymer in the synthesized composite was estimated by

thermogravimetric analysis. A comparison of thermograms for the parent saponite and modified one (see Figure. 3) proved that the most of the immobilized copolymer decomposes at the temperature range 150-630 °C and about 18.5 wt.% of the composite is lost.

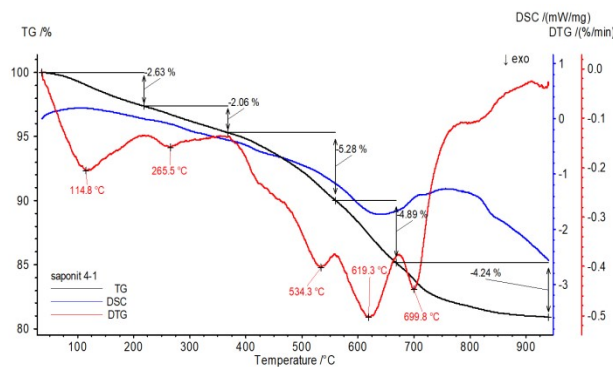


Figure 3. TG, DTG and DSC curves of the modified saponite

Taking into account that parent saponite loses 10 wt.% [6, 7] at this temperature, it can be concluded that the mass fraction of copolymer in the synthesized material is 8.5 wt.%.

As could be expected, the immobilized copolymer is destroyed at the temperature region 500-650 °C with the formation of CO₂ and N₂O what is confirmed with the mass spectrometry data. The most intense signal locates at 44 Da (CO₂ and N₂O) and overlap with a signal at 28 Da of CO and nitrogen, expected formation of water could be detected at 18 Da (see Figure. 4, 5). Signals at 16, 32 and 34 Da could be attributed to the formation of such destruction products as CH₄, C₂H₆ and C₂H₄.

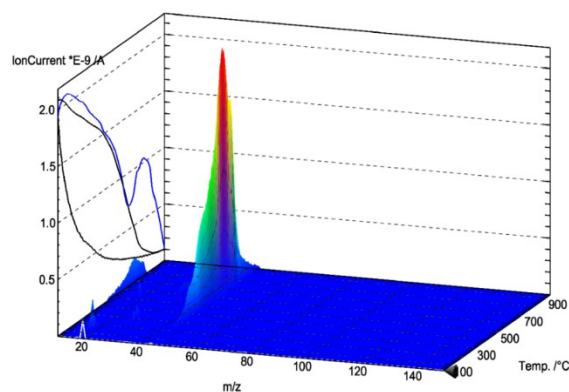


Figure 4. TG-MS-3D of the modified saponite

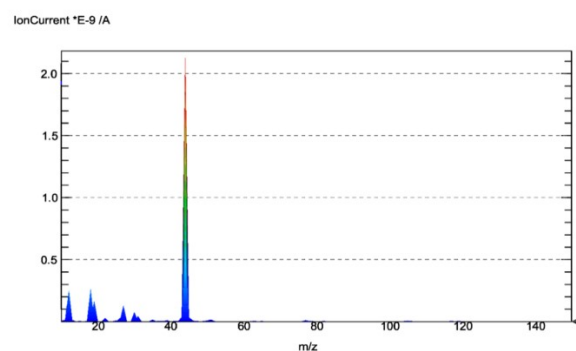
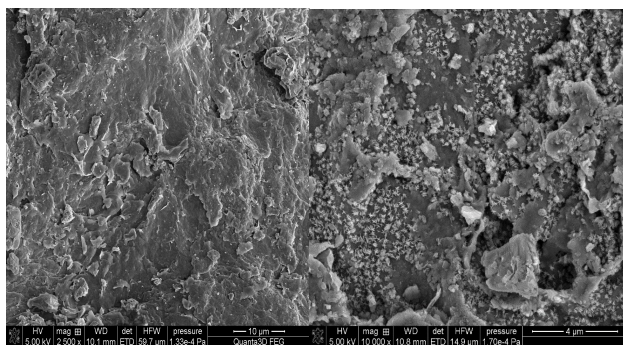


Figure 5. 2D mass spectrum of the modified saponite (T= 600°C)

Computer data processing of nitrogen adsorption/desorption isotherms by the BJH method indicated a decrease in the specific surface area of parent saponite from 41 m²/g to 3 m²/g for saponite with surface-immobilized copolymer. The surface of the modified saponite remains mainly mesoporous. However, pore size and total volume decrease.

Changes in the morphology of saponite with surface-immobilized copolymer in comparison with non-modified mineral was recognized by scanning electron microscopy. The SEM-photos of the surface are shown on Figure 6.



a b

Figure 6. SEM-image of the surface of the parent (a) and modified (b) saponite

As seen from the photographs presented, the copolymer is placed unevenly on the surface of the mineral in the form of elongated and circled spiral chains. Obviously, such a location of the copolymer on the surface only partially affects on the morphology of mineral carrier. Thus, the scanning electron microscopy data are in good agreement with the surface parameters calculated by the BJH method.

The study of the adsorption capacity of the synthesized composite towards Cu(II), Cd(II), Pb(II), Mn(II) and Fe(III) ions included:

- establishing the time of the phase contact that required to achieve the sorption equilibrium in the static sorption mode;
- sorption isotherms plotting for each metal ion;
- estimation of the sorption capacity for each metal ion and comparison with the original saponite.

A sorption activity towards Cd(II) ions was not detected neither for saponite nor for the silica gel with immobilized copolymer of 4-vinylpyridine and styrene[14]. However,

saponite *in situ* modified with some other Nitrogen-containing organic polymers exhibited sorption activity towards Cd(II) ions [16]. As it was found, sorption activity to Cd(II) ions of Saponite with immobilized 4-vinylpyridine-*co*-styrene polymers negligible.

The dependences of the sorption degree of Cu(II), Pb(II), Mn(II) and Fe(III) ions on the modified saponite surface from the static contact time indicate that all the ions were absorbed after 24h contact and then sorption equilibrium is reached. Such a behavior is more close to organic polymeric sorbents in comparison with inorganic materials. Quantitative sorption was found for the micro quantities of Cu(II) and Fe(III) ions. However, as can be seen from Figure 7, the maximum Cu(II) and Pb(II) ions is removed during the first minutes of contact with the sorbent. In addition, that composite exhibits low sorption capacity towards Mn(II) ions.

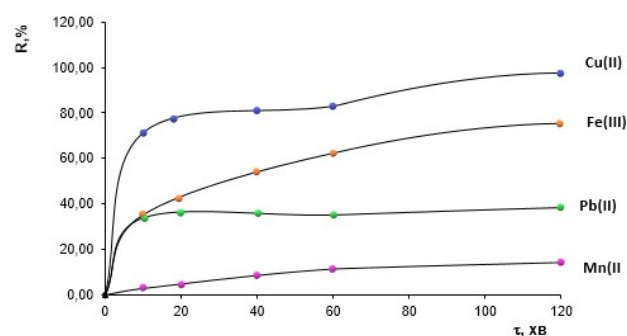


Figure 7. Dependence of Cu(II), Pb(II), Mn(II), Fe(III) ions adsorption degree from the contact time with modified saponite in static mode. Experimental conditions: composite mass 0.1 g, volume of solution 25 ml, $m_M^0 = 100 \mu\text{g}$.

In order to determine the values of sorption capacity of modified Saponite in

comparison with parent mineral, the sorption isotherms were plotted. All of the isotherms obtained belong to the 2L-type and allow you to calculate the adsorption capacity for the parent and modified Saponite.

The values of the sorption capacity for the Cu(II), Pb(II), Fe(III) and Mn(II) ions were calculated from the sorption isotherms and are given in comparison with literature data in Table 1. As one can see, the sorption capacity of saponite after surface modification with 4-vinylpyridine-*co*-styrene polymer increases by 29%, 21% and 13% compared to Cu(II), Fe(III) and Pb(II) ions respectively. This growth can be explained by complexation of metals with pyridine moiety of an immobilized copolymer. Since the stability of pyridine complexes of Cu(II) and Fe(III) is higher than for Pb(II) ions, it increases the sorption capacity of the composite towards Cu(II) and Fe(III) ions.

Table 1. Adsorption capacity of parent mineral saponite and *in situ* modified saponite towards of Cu(II), Mn(II), Pb(II) and Fe(III) ions

Cation	Adsorption capacity			
	Parent Saponite		Modified Saponite	
	mM/g	mg/g	mM/g	mg/g
Fe(III)	0.014[16]	0.78	0.017	0.95
Pb(II)	0.016[16]	3.31	0.018	3.73
Mn(II)	0.016	0.88	0.017	0.94
Cu(II)	0.017[16]	1.09	0.022	1.41

As follows from Table 1, the growth of sorption capacity of modified saponite in comparison with the parent mineral towards Mn(II) ions is within the experimental error. Thus, surface modification of saponite with an organic polymer 4-vinylpyridine-*co*-styrene does not lead to an improvement in the sorption capacity towards Mn(II) ions.

Conclusions

In situ modification of saponite, a mineral from Tashkivske deposit, Ukraine, was carried out by precipitated radical copolymerization of 4-vinylpyridine and styrene with molar ratio 3:1 in an organic solvent CCl₄. The amount of immobilized copolymer in the composite in accordance with thermogravimetry data is 8.5 ± 0.5 wt.%. FT-IR, MS and SEM data prove a formation of organo-mineral composite.

The copolymer is located on the mineral surface in a form of elongated and twisted chains. Nitrogen adsorption/desorption isotherms processed by BJH method elucidate a decrease in the surface area, pore size and pore volume of the saponite surface as a result of copolymer immobilization. It was revealed that the surface of the modified mineral remains mainly mesoporous.

A comparison of the adsorption properties of the parent and modified saponite towards Cu(II), Cd(II), Pb(II), Mn(II) and Fe(III) ions detect a slight increase in the

sorption capacity of modified Saponite to Cu(II), Pb(II) and Fe(III) ions.

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