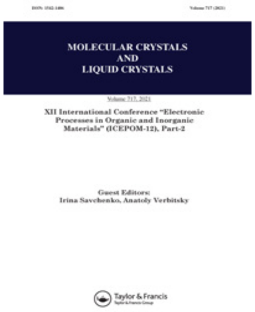

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Adsorption properties of natural alumosilicate Ukrainian minerals, *in situ* modified by poly[8-methacroyloxyquinoline] to Pb(II), Mn(II), Cu(II) and Fe(III) ions

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ABSTRACT

Immobilization of poly[8-methacroyloxy-quinoline] on a natural saponite surface immediately after polymer formation has been performed. The adsorption properties of the modified adsorbent with respect to Cu(II), Pb(II), Mn(II) and Fe(III) were studied. As a result of thermogravimetric analysis and DSC-MS analysis, it has been found that the composition of synthesized composite includes 10.14 wt% of polymer. As a result of the comparison of the sorption properties of the modified and original minerals with respect to the Pb (II), Cu (II), Mn (II) and Fe (III) ions, their improvement was recorded after modification by the polymer selected with respect to the ions Pb (II), Fe (III) and Cu (II).

KEYWORDS

adsorption; in situ immobilization; saponite; poly[8-methacroyloxy-quinoline]; composite; heavy metals

1. Introduction

Environmental pollutants and their toxicity cause a major problem worldwide. New pollutants keep emerging and pose severe health and scientific challenges. Water pollution is one of the biggest environmental issues causing serious problems to living beings. The removal of various toxic substances from water and wastewater has been a core interest of many scientists and researchers around the globe over the past decades [1–3].

Nano clay composites such as or organoclays, polymer–clay nanocomposites, are an attractive class of hybrid organic–inorganic nanomaterials. Polymer–clay nanocomposite is a matter of an increased interest in research and development around the globe based on their capacity for selective adsorption of molecules and to solve water problems.

Most heavy metals are known to be carcinogenic agents and may represent a serious threat to the living population because of their nondegradable, persistent and accumulative nature [4,5].

Adsorption process is a suitable technique for inorganic and organic pollutants removal from wastewater, because of the significant advantages like low-cost, availability, profitability, ease of operation, efficiency and effectiveness than other techniques [6,7].

This technique is easy to operate and equally effective in the removal of toxic pollutants, even at low concentrations. Clay, a fine-grained natural raw material, is a matter

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of much attention due to its use as an effective adsorbent to trace heavy metal ions present in aqueous solution for more than a decade now [8]. Clay minerals have space between their layers, which is the main reason they adsorb toxic metals that are present in water molecules. Most of the clays can swell and increase the space between their layers to accommodate the adsorbed water and ionic species.

The natural minerals of Ukraine, widely known for their sorption properties in relation to various anthropogenic substances, include Ukraine saponite [9]. To improve the sorption properties of natural minerals, it is expedient to modify their surface with substances capable of complexation and ion exchange, in particular nitrogen- and oxygen-containing polymers.

One of the ways to immobilize polymers on solid surfaces is the *in situ* method of polymerization, which allows "to grow" a polymeric film directly on the surface of the carrier in the process of polymer synthesis [10,11]. *In situ* polymerization involves two interconnected processes: the chemical process is the growth of macromolecules and the physical – self-assembly of growing chains in complex supramolecular structures. As a result, an ordered layer of polymer is formed, which is strongly adsorbed on the surface of the carrier.

The *in situ* polymerization method can be successfully applied to carriers of different shapes and rigidity. Moreover, it is the only way to obtain a polymer layer on porous and powdered nanoscale carriers. The advantage of this method of immobilizing polymers on solid surfaces is universality with respect to the chemical nature of the carrier [12].

As it follows from the review of modern literary sources [13,14], the laws of physical and chemical fixation of polymers on the surface of carriers of different chemical nature in order to obtain substances with new interesting and useful properties are not fully understood and their research is relevant today.

This work is devoted to the modification of the saponite surface of the Tashkiv deposit of Ukraine, by poly[8-methacroyloxy-quinoline] by *in situ* polymerization and the study of sorption properties of the modified mineral in relation to toxic metals ions such as Cu (II), Pb (II), Mn (II) and Fe (III).

2. Experimental

2.1. Materials

As a mineral porous base for polymer modification used saponite of Tashkiv deposit of Slavutsky district of Khmelnitsky region, chemical composition and physicochemical properties of which are described in the paper [15].

The synthesis of 8-methacroyloxy-quinoline is given below: 8-hydroxyquinoline (18.15 g, 0.0125 mol) was dissolved in 100 mL anhydrous THF, and freshly distilled triethylamine (34.78 mL, 0.25 mol) was added to the solution. The reaction mixture was then cooled to 0–5 °C. Methacryloyl chloride (24.41 mL, 0.25 mol) in THF (50 mL) was injected gradually to the above solution via a glass syringe while the solution temperature was kept below 5 °C. The reaction mixture was stirred overnight at room temperature. The resulting precipitate was filtered off. Purification was followed by recrystallization from methanol. Yield: 86%.

8-Methacroyloxy-quinoline. ^{1}H NMR (400 MHz, DMSO, δ, ppm): δ 7.48–7.59 (t, 3H), 8.85–7.85 (s, 2H), 6.40 (s, 1H $C=CH_2$, cis), 5.85 (s, 1H $C=CH_2$, trans), 2.11 (s, 3H, $=C\text{-}CH_3$).

The polymerization of 8-methacroyloxy-quinoline in the presence of saponite (fraction of particles with a diameter of 0.1–0.2 mm, specific surface 428.61 m^2/g, Merck) has been ccarried out under the argon atmosphere. A solution of 6.5 g 8-methacroyloxy-quinoline and 0.065 g of 2,2′-azobisisobutyronitrile (AIBN) in 150 mL tetrahydrofuran (THF) were poured into a flask containing 19.5 g of silica gel. When argon blowing was finished after 15 min, the reaction mixture was heated to 78 °C; polymerization continued for 5 h with stirring. The reaction was stopped by cooling the reaction mixture. The resulting suspension was poured into a porcelain cup and left overnight to evaporate the solvent; the synthesized composite was washed three times with isopropyl alcohol, filtered and air-dried for 24 h at room temperature.

FTIR spectra of the samples of composite and the original mineral were recorded using an IR spectrometer with Fourier transformation (Thermo Nicolet Nexus FT-IR, USA). For this purpose the samples were ground in an agate mortar and pressed with KBr. The FTIR spectra were recorded in the spectral range of 500–4000 cm^{-1} with 16 scans per spectrum at a resolution of 4 cm^{-1}.

2.1.1. Thermal analysis

Thermal analysis was carried out on a STA 449 Jupiter F1, Netzsch (Germany) under the following operational conditions: heating rate of 10 °C min^{-1}, dynamic atmosphere of synthetic air (50 mL min^{-1}), temperature range of 30–950 °C, sample mass approximately 18 mg, sensor thermocouple type S TG-DSC. As a reference empty Al_2O_3 crucible was used. The gaseous products emitted during decomposition of material were analyzed by QMS 403C (Germany) coupling on-line to STA instrument. The QMS data were gathered in the range from 10 to 160 amu.

2.1.2. Surface morphology analysis

The surface morphology of composite was observed by a scanning electron microscope (SEM, LEO 1430VP, Carl Zeiss, Germany).

2.1.3. The investigations of adsorption properties

Properties of the obtained composite to adsorb Cu(II), Pb(II), Mn(II), Fe(III) were studied in static mode. Working solutions of the nitrates of corresponding metals were prepared using volumetric flasks of 25 mL, 50 or 100 mL, diluting solutions to the mark with standard buffer solutions of certain pH values, and then, the required volume was added to flat-bottom flasks containing 0.1 g of the adsorbent. The reaction was proceeding while the flasks were shaken mechanically. Equilibrium concentrations of ions were measured using atomic absorption methods.

Working nitrate solutions of Cu(II), Mn(II), Fe(III) are prepared with the sets of “standard sample solutions” of these salts on 1 M HNO_3 background (produced by A.V. Bogatsky FHI in Odesa) with concentrations of 1 and 10 mg/mL.

To create pH 4.0, a standard phtalate buffer solution was prepared using a titration substance (ISO 8,135: 2009, manufacturer - JSC “Kyiv Plant RIAP”). To prepare a buffer ammonia-acetate solution at pH 8.4, 17 mL of 0.1 M acetic acid was poured into a 1 L volumetric flask and 5 mL of 6.5 M (25%) of ammonia solution was added. The exact pH was measured using a pH meter “HANNAHI 98129,” adding dropwise acetic acid or ammonia solution. The resulting solution was brought to the mark with distilled water.

The speed of the establishment of the sorption equilibrium was determined by the following procedure: the working solutions of metal salts with an optimal pH value of 25 mL containing 100 μg of metal ion were shaken from 0.1 g of sorbent for 5–90 min. After sorption for 5, 10, 20, 30, 60 and 90 min of contact, aliquot volumes of equilibrium solutions were selected and their concentration of metal ions was determined.

Determination of the equilibrium concentration of the metals was carried out by atomic absorption using a flaming atomic absorption spectrophotometer “Saturn” (Ukraine) in a “air - propane – butane” flame mixture. Maxima wavelengths were: 324.7 nm for Cu(II), 228.8 nm – for Cd(II), 283.3 nm – for Pb(II), 248.3 nm – for Fe(III), aperture being 0.5 cm wide.

2.2. Calculations

The adsorption capacity (A) was calculated using the formula:

$$A = (c_o – [\mathbf{M}])\ V/m$$

where c_o – the initial molar concentration of the metal, $[M]$ is the equilibrium molar concentration of the metal, V – is the volume of the working solution (l) , m – is mass of the adsorbent (g).

The adsorption rate (R) was calculated according to the equation:

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

where m_o – is mass of metal in the starting solution (mkg), $m_{\mathbf{ads}}$ – is mass of the metal adsorbed, $[m]$ – is mass of the metal at equilibrium after the adsorption, which was found $[m]$=C$\cdot V$, where C – is concentration of the metal at equilibrium (mrg/mL) and V – is the volume of the solution at equilibrium (mL).

3. Results and discussion

3.1. Physicochemical characteristics of the synthesized composite

The chemical structure of *in situ* polymer immobilization 8-methacroyloxy-quinoline on the saponite surface could be presented as follows (Fig. 1):

The fact of the process of *in situ* polymerization and fixing of the polymer on the saponite surface were confirmed by comparative analysis of IR spectra of original mineral (A) and modified mineral (Fig. 2).

A comparative analysis of the IR spectra of the synthesized composite and its original mineral carriers shows that, in contrast to the original mineral, a number of new absorption bands are observed in the spectrum of composite. The most informative to confirm the

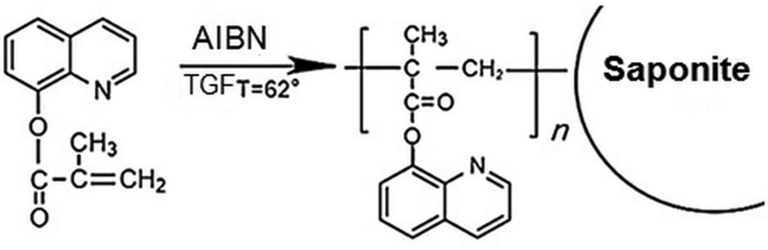

Figure 1. The scheme of *in situ* immobilization of poly[8-methacroyloxy-quinoline] on the saponite surface.

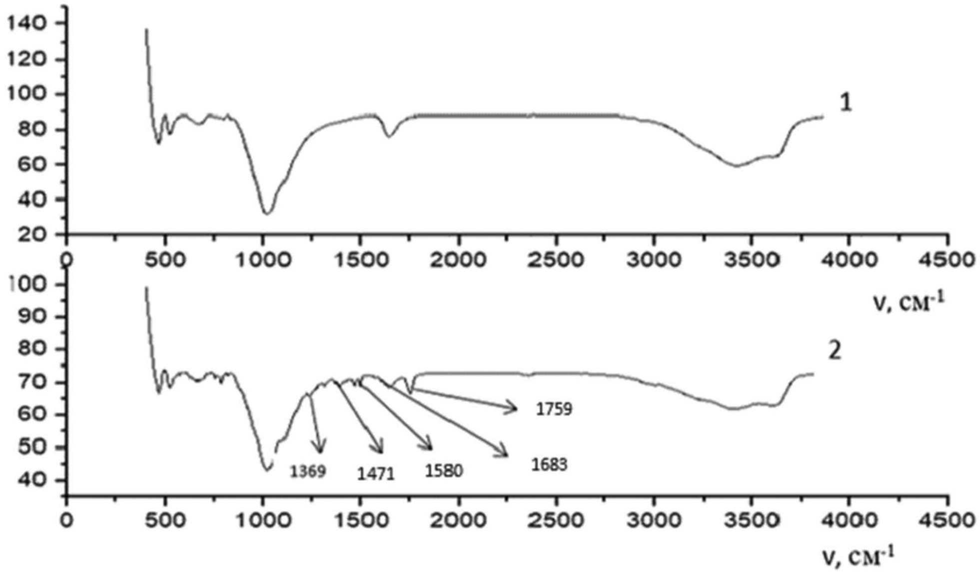

Figure 2. IR spectra of the original (1) and modified saponite (2).

presence of poly [8-oxyquinolinomethacrylate] in the surface layer of selected mineral are a number of bands in the region 1200–1700 cm^{-1}, which can be interpreted as follows:

- vibrations in the region 1578–1683 cm^{-1} may correspond to the valence vibrations υ (C = N) and υ (C = C) of the aromatic quinoline system;
- absorption band at 1759 cm^{-1} can be attributed to the valence vibrations υ (Ar-COO-R);
- absorption bands in the range from 1361 to 1479 cm^{-1} correspond to the skeletal oscillations of the C-C bonds of the aromatic quinoline system.

The presence of these absorption bands in the IR spectrum of the synthesized composite may be evidence of the presence of poly [8-oxyquinoline methacrylate] in their composition.

To determine the mass of the immobilized polymer, a thermogravimetric analysis of the original and modified saponite was performed. The obtained thermograms are shown in Figs. 3 and 4. From these figures, it is seen that the predominant amount of

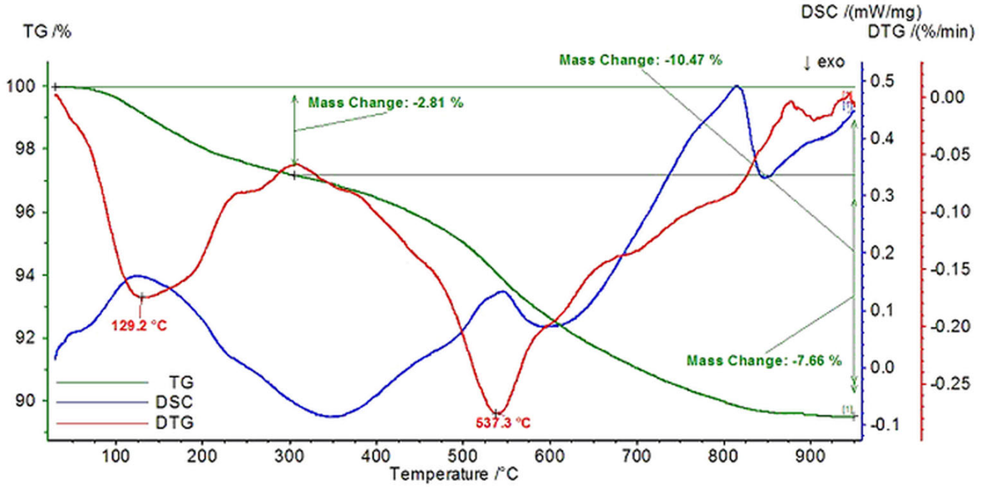

Figure 3. Thermogram of the original saponite.

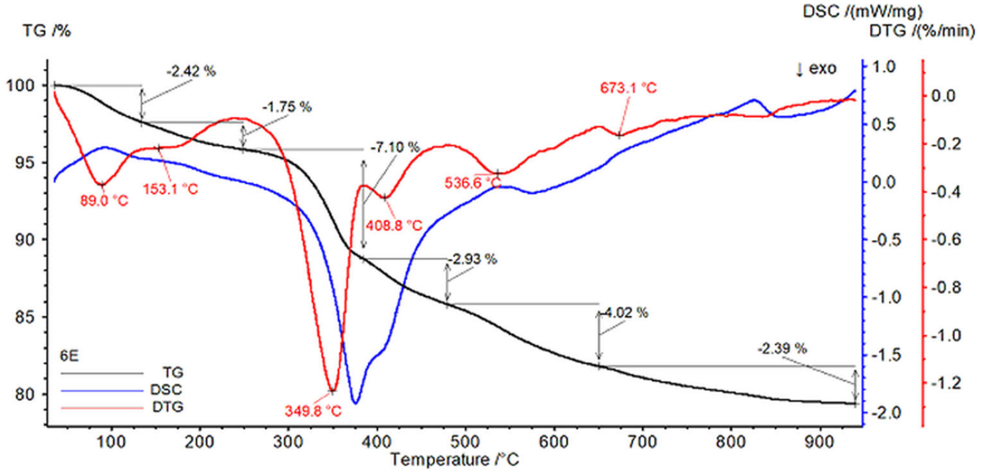

Figure 4. Thermogram of the modified saponite.

immobilized polymer decomposes in a temperature range of 89 to 700 °C. 20.61% of its mass is lost. The weight loss of the original mineral in this temperature range is 10.47%, respectively (Fig. 3). Therefore, the weight of the immobilized polymer in the composition of composite is 10.14%.

To detail the process of thermo destruction of the composite, its thermogram, combined with mass spectrum, was obtained in 3D format (Fig. 5a), Mass spectrum 2D format (Fig. 5b) and thermogram combined with infrared spectrum, in 3D format (Fig. 5c).

As can be seen from these figures, the thermal destruction of the composite occurs with the formation of water and carbon dioxide, as evidenced by the high-intensity peaks corresponding to masses 18 and 44. However, in the mass spectra of this composite there is also a low-intensity peak at mass 28, which most likely corresponds the formation of carbon (II) oxide or nitrogen.

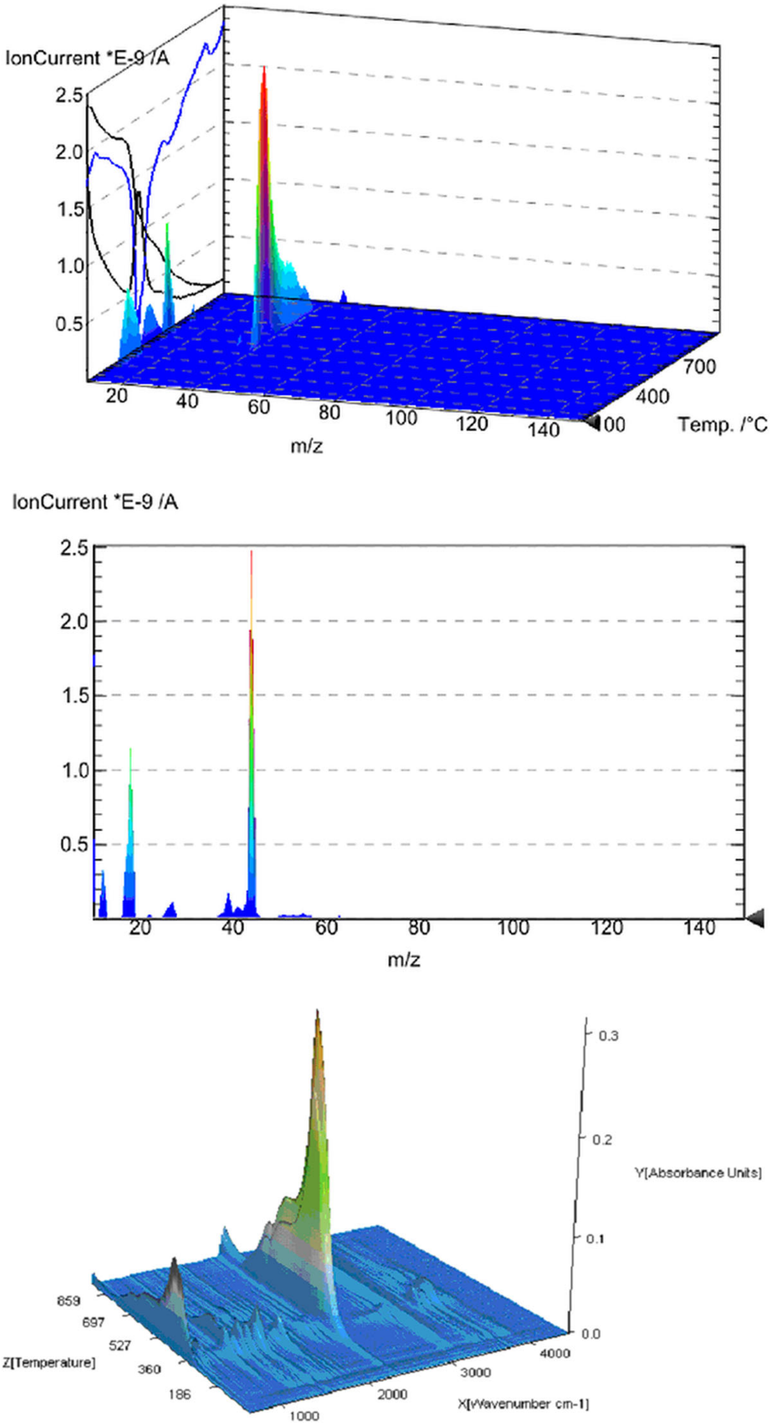

Figure 5. (a). TG-MS-3D of the synthesized composite. (b). MS-2D of the synthesized composite. (c). Thermogram combined with infrared spectrum, in 3D format (C) of the synthesized composite.

Table 1. Characteristics of the surface of saponite and synthesized composite.

Sample	Surface area (m^2/g) P/P_0	BET	Langmuir	Average pore volume (cm^3/g)	Average pore size (nm)
Saponite	41.01	41.48	64.85	0.085	8.21
Composite	1.89	1.86	2.28	0.011	22.49

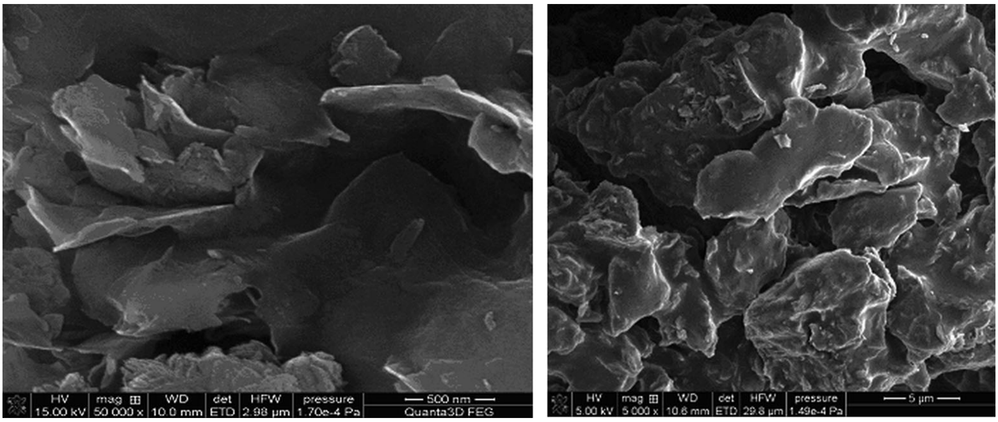

Figure 6. (a) CEM photo of the surface of the original saponite at an increase of 50,000 times. (b) CEM photo of the surface of the composite at an increase of 5000 times.

To investigate the parameters of the surface of synthesized composites, the method of BET (low-temperature adsorption-desorption of nitrogen) was used.

The resulting adsorption-desorption nitrogen isotherms for the original saponite and the synthesized composite are similar and belong to the type IV isoterm according to the classification of *IUPAC* [16]. This suggests that the structure of the surface of mineral as a result of fixing the polymer is unchanged practically.

The surface area, average volume, and pore size of the surface of the synthesized composite, calculated by computerized isotherm processing, are shown in Table 1.

From the data in Table 1, it follows that as a result of immobilization of poly [8-oxyquinolinomethacrylate] on the surface of the saponite.

- specific surface area decreases by 21.7 times.
- average pore volume decreases by 7.7 times.
- average pore diameter increases 2.7 times for saponite.

The established changes in the surface parameters of the selected mineral are logical consequences of its modification by the polymer and at the same time serve as additional confirmation of such modification.

The surface of saponite before and after modification by a polymer was investigated by scanning electron microscopy (Figs. 6–8). As can be seen from the obtained photos, the polymer is on the surface of the mineral in the form of convex agglomerates. The modification of the polymer does not change the structure of the mineral surface, but only reduces its porosity.

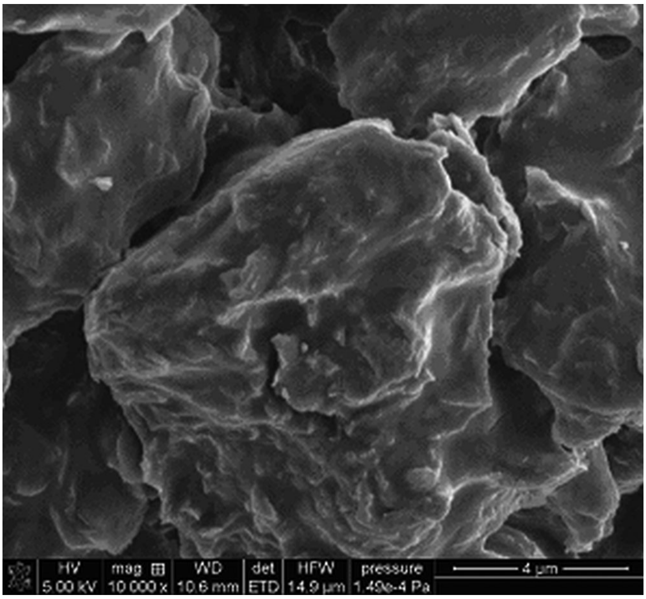

Figure 7. CEM photo of the surface of the composite at an increase of 10,000 times.

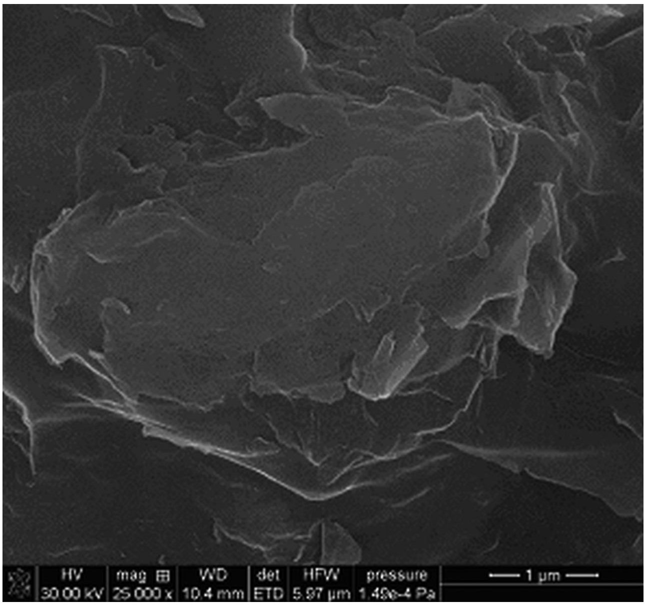

Figure 8. CEM photo of the surface of the composite at an increase of 25,000 times.

Since the immobilized polymer is composed of 8-oxyquinoline groups, it must exhibit complex-forming activity with respect to transition metal ions due to nitrogen oxide. To confirm these considerations, we investigated the sorption of transition metal ions with a high affinity for nitrogen-containing ligands.

Investigation of the sorption capacity of the synthesized composite for these metal ions included:

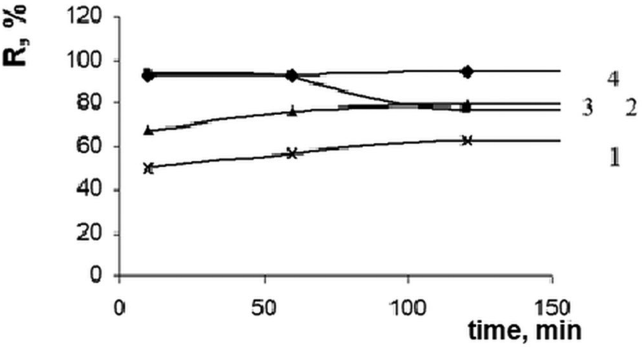

Figure 9. Kinetics of sorption of Mn^{2+} (1), Cu^{2+} (2), Fe^{3+} (3), Pb^{2+}(4) ions on the surface of saponite, *in situ* modified poly [8-methacroyloxy-quinoline].

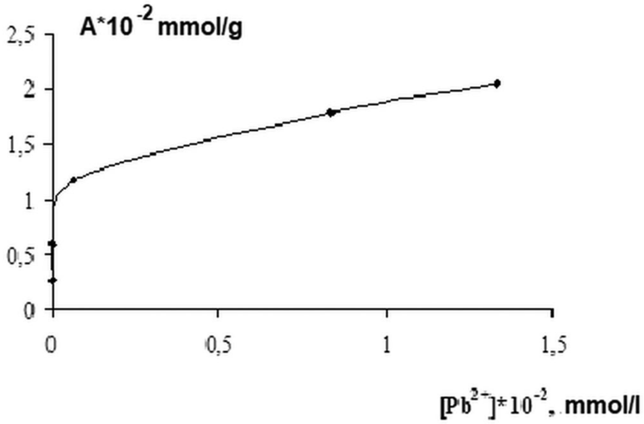

Figure 10. Adsorption isotherm of ions Pb(II) on saponite surface with immobilized poly [8-methacroyloxy-quinoline].

- study of the rate of sorption of selected ions on the surface of the synthesized composite in static mode from aqueous nitrate solutions;
- construction of isotherms of sorption of each of the investigated metal ions on the surface of the synthesized composite;
- determination of sorption capacity for each of the investigated metal ions and comparison with the original mineral.

The kinetics of sorption of selected metal ions by the composite surface is presented in Fig. 9.

As can be seen from Fig. 9, the optimal sorption time of Cu (II) and Pb (II) ions on the surface of the composite in static mode is 1 h, and the Fe (III) and Mn (II) ions are 2 h. The optimum contact time of all metal ions with the composite surface was taken into account during the experiments of sorption isotherm construction.

To determine the sorption capacity of the composite relative to the selected transition metal ions, their sorption isotherms were constructed (Figs. 10–13).

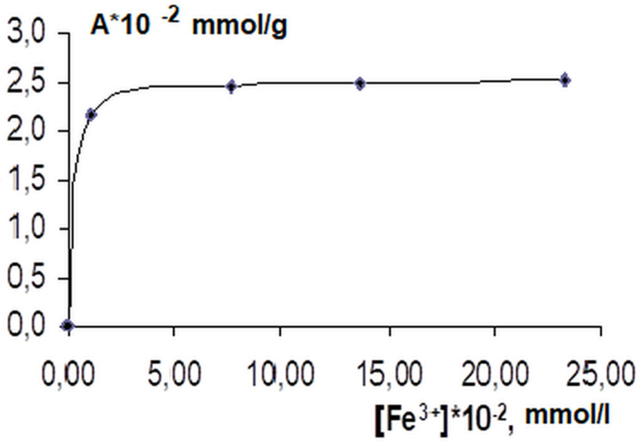

Figure 11. Adsorption isotherm of ions Fe(II) on saponite surface with immobilized poly [8-methacroyloxy-quinoline].

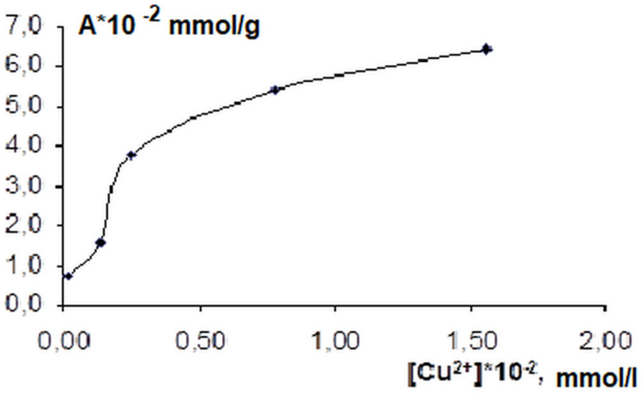

Figure 12. Adsorption isotherm of ions Cu(II) on saponite surface with immobilized poly [8-methacroyloxy-quinoline].

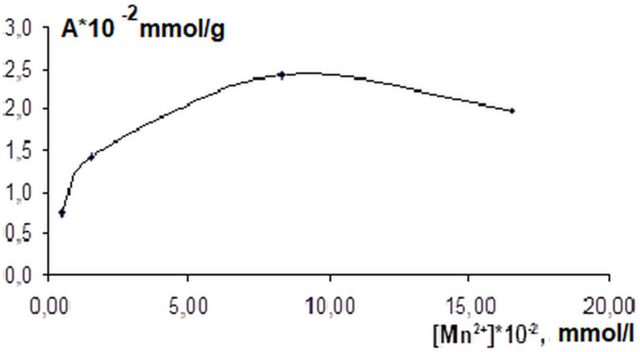

Figure 13. Adsorption isotherm of ions Mn(II) on saponite surface with immobilized poly [8-methacroyloxy-quinoline].

Table 2 Adsorption capacity of the original mineral and the synthesized composite.

Cation	Adsorption capacity Original mineral mmol/g	Composite mmol/g
Cu^{2+}	0.017	0.064
Fe^{3+}	0.014	0.025
Pb^{2+}	0.016	0.021
Mn^{2+}	0.015	0.015

The values of the sorption capacity of the original mineral and the synthesized composite relative to the ions Pb (II), Fe (III), Cu (II) and Mn (II), calculated from the sorption isotherms, are presented in Table 2.

As follows from Table 2, the sorption capacity of the selected mineral after modification of poly [8-oxyquinolinomethacrylate], unlike modified silica gel:

- significantly increases with respect to Cu (II) ions: 3.8 times;
- increases with respect to Pb (II) ions: – by 30%;
- does not change with respect to Mn (II) ions.

The sorption capacity for Fe ions (III) increases 3.8 times.

Of course, the results can be explained by the processes of complexation of metal ions with poly [8-oxyquinolinomethacrylate] molecules, since they correlate well with the stability constants of these ions with 8-oxyquinoline.

4. Conclusions

In summary, a new hybrid organic/inorganic composite has been synthesized by *in situ* immobilization of poly [8-methacroyloxy-quinoline] on the surface of saponite (Ukraine) surface. The fact of polymer immobilization has been confirmed by IR spectroscopy. As a result of thermogravimetric analysis and DSC-MS analysis it has been found that the composition of synthesized composite includes 10.14 wt. % of polymer. As a result of the comparison of the sorption properties of the modified and original minerals with respect to the Pb (II), Cu (II), Mn (II) and Fe (III) ions, their improvement was recorded after modification by the polymer selected with respect to the ions Pb (II), Fe (III) and Cu (II).

For the future, low-cost adsorbents, such as natural and modified clays, show great promise. The applications of natural and modified clays in commercial wastewater treatment are expected to be significant.

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