

# Synthesis of an organo-inorganic composite based on clinoptilolite (Ukraine) *in situ* modified by poly [8-oxyquinoline methacrylate] and its sorption properties with respect to toxic metal ions

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*Received March 10, 2021*

A new organo-mineral composite material was obtained by *in situ* immobilization of poly [8-oxyquinoline methacrylate] on the surface of clinoptilolite (Ukraine). The fact of immobilization of the polymer on the mineral surface was confirmed by IR spectroscopy and thermogravimetric analysis combined with mass spectrometry. As a result of comparing the sorption properties of the synthesized composite and the original mineral with respect to  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  ions, their improvement after modification by the selected polymer with respect to  $\text{Pb(II)}$  and  $\text{Cu(II)}$  ions was recorded.

**Keywords:** adsorption, *in situ* immobilization, clinoptilolite, poly[8-oxyquinoline methacrylate], organo-mineral composite.

**Синтез та сорбційні властивості органо-неорганічного композиту на основі кліноптилоліту (Україна), *in situ* модифікованого полі[8-оксихінолінметакрилатом], щодо йонів токсичних металів. І.О.Савченко, Е.С.Яновська, Д.Стернік, О.Ю.Кичкирук**

Шляхом *in situ* іммобілізації полі[8-оксихінолінметакрилату] на поверхні кліноптилоліту (Україна) отримано новий органо-мінеральний композиційний матеріал. Факт іммобілізації полімеру на поверхні мінералу підтверджено методами ІЧ-спектроскопії та термогравіметричного аналізу, об'єднаного з мас-спектрометрією. У результаті порівняння сорбційних властивостей синтезованого композиту і вихідного мінералу щодо йонів  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Mn}^{2+}$  та  $\text{Fe}^{3+}$  зафіксовано їх покращення після модифікації обраним полімером щодо йонів  $\text{Pb(II)}$  та  $\text{Cu(II)}$ .

Методом *in situ* іммобілізації полі[8-оксихінолінметакрилата] на поверхності кліноптилоліта (Україна) отримано новий органо-мінеральний композиційний матеріал. Факт іммобілізації полімера на поверхності мінерала підтверджено методами ІЧ-спектроскопії та термогравіметричного аналізу, об'єднаного з мас-спектрометрією. В результаті порівняння сорбційних властивостей синтезованого композита і вихідного мінерала по відношенню к іонам  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Mn}^{2+}$  и  $\text{Fe}^{3+}$  зафіксовано их улучшение после модификации выбранным полимером по отношению к ионам  $\text{Pb(II)}$  и  $\text{Cu(II)}$ .

## 1. Introduction

One of the important environmental tasks is the treatment of industrial wastewater from instrument-making and galvanic industries, which contain heavy metal ions in concentrations much higher than the maximum allowable. Heavy metals have a negative effect on living organisms because they are highly toxic. Therefore, wastewater from the production cycles of instrument-making and galvanic industries requires constant monitoring, as well as the development of effective cheap and environmentally friendly technologies for the removal of toxicants, which, in particular, include sorption methods. For these reasons, the use of effective and safe sorbents with high selectivity will ensure the rational use of water resources, compliance with environmental standards. Such requirements are met by materials based on clay minerals, which are characterized by relative cheapness, environmental friendliness and general availability. Clay minerals due to the significant dispersion of the particles and the presence of a large number of sorption centers on their surface, show good adsorption properties, as well as the ability to cation exchange.

Transcarpathian clinoptilolites belong to the natural minerals of Ukraine, widely known for their sorption properties against various anthropogenic substances [1, 2]. To improve the sorption properties of natural minerals, it is advisable to modify their surface with substances that are capable of complexation and ion exchange, in particular nitrogen- and oxygen-containing polymers [3–5]. Such composites are characterized by chemical activity against both cations and anions of heavy metals, due to the simultaneous action of several sorption mechanisms: extraction into the pores, ion exchange and the formation of complexes. The obtained sorbents can be used both in wastewater treatment and directly for groundwater treatment in places near sources of pollution [6, 7].

One of the ways of immobilization of polymers on solid surfaces is the method of *in situ* polymerization, which allows you to "grow" the polymer film directly on the surface of the matrix in the process of polymer synthesis. *In situ* polymerization includes two interrelated processes: the chemical process of the growth of macromolecules and the physical process of the self-assembly of growing chains into complex supramolecular structures. As a result,

an ordered layer of polymer is formed, which is firmly adsorbed on the surface of the matrix. The *in situ* polymerization method can be successfully applied to matrices of different shapes and stiffness. Moreover, it is the only way to obtain a polymer layer on porous and powdered nanosized matrices. The advantage of this method of immobilization of polymers on hard surfaces is the versatility of the chemical nature of the matrix [8].

In [9, 10] it was shown that *in situ* immobilization of the surface of Podolsk saponite and Sokyrnytsia clinoptilolite with polyaniline leads to an increase in the sorption capacity of these minerals relative to phosphate and arsenate ions in a neutral aqueous medium by a factor of 2–3. And *in situ* immobilization of the surface of saponite of the Tashkovsky deposit [11] and clinoptilolite of the Tushinsky deposit [12] by such complexing polymers as poly [N-(4-carboxyphenyl) methacrylamide] or poly [4-methacryloxy-(4'-carboxy-2'-nitro) azobenzene] increases their sorption capacity in a neutral aqueous medium relative to ions Pb(II), Cd(II), Cu(II) and Fe(III). In [13], the sorption properties of saponite *in situ* modified with poly [4-methacryloxy-(4'-carboxy-2'-nitro) azobenzene] relative to heavy metal ions were investigated, and an increase in sorption capacity was recorded several times.

This work is devoted to *in situ* immobilization of poly [8-oxyquinoline methacrylate] on the surface of clinoptilolite of the Tushinsky deposit and study of sorption properties of the synthesized composite material against ions of such toxic metals as Cu(II), Pb(II), Mn(II) and Fe(III).

## 2. Experimental

Clinoptilolite of the Tushinsky deposit, located in the Transcarpathian region of Ukraine, which was used as an inorganic matrix of the composite, had the following parameters: chemical formula is  $\text{Na}[\text{AlSi}_5\text{O}_{12}]\cdot 6\text{H}_2\text{O}$ ; chemical composition (in wt.%):  $\text{SiO}_2$  — 67.07;  $\text{Al}_2\text{O}_3$  — 12.4;  $\text{K}_2\text{O}$  — 2.8;  $\text{CaO}$  — 2.09;  $\text{Na}_2\text{O}$  — 2.05;  $\text{Fe}_2\text{O}_3$  — 0.9;  $\text{FeO}$  — 0.76;  $\text{TiO}_2$  — 0.19;  $\text{P}_2\text{O}_5$  — 0.117;  $\text{MgO}$  — 0.072;  $\text{MnO}$  — 0.07;  $\text{SO}_3$  — 0.08; porosity is 45 %; the average pore diameter is 50 nm, the specific surface area is 22  $\text{m}^2/\text{g}$ .

The monomer — 8-oxyquinoline methacrylate — was synthesized according to the following method: 8-hydroxyquinoline (18.15 g, 0.125 mol) was dissolved in 100 ml anhy-

drous 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.

8-oxyquinoline methacrylate  $^1\text{H}$  NMR (DMSO): d 7.483–7.593(t, 3HH), 8.850–7.849 (c, 2H), 2.110(c, 3HH), 3.136–2.490 (d, 2H), 5.85 (c, 1H), 6.4 (c, 1H).

In situ immobilization of poly [8-oxyquinoline methacrylate] on the surface of clinoptilolite was carried out according to the following method. The polymerization of 8-methacroyloxy-quinoline in the presence of clinoptilolite has been carried 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 clinoptilolite. 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 3 times with isopropyl alcohol, filtered and air-dried for 24 h at room temperature.

The IR spectra of the original clinoptilolite and the synthesized composite of the same mass were recorded on an IR spectrometer "Spectrum BX" (Perkin Elmer, Germany) in the range of 500–4000  $\text{cm}^{-1}$  in KBr tablets.

The amount of immobilized polymer on the surface of the modified mineral was evaluated by thermogravimetric analysis using a synchronous TG/DTA analyzer "Shimadzu DTG-60 H" (Shimadzu, Japan) in the temperature range of 15–1000°C. The heating rate of the samples was 10 deg/min. Differential scanning calorimetry was performed on an instrument "STA 449 Jupiter F1" (Netzsch, Germany) with a mass spectroscopic attachment "QMS 403C" (Germany).

The specific surface area and mean pore diameter were calculated from low-temperature nitrogen adsorption/desorption isotherms using the software of the ASAP 2420 V1.01 sorbometer (Micromeritics,

USA). Before measurements, the samples were degassed at 60°C for 24 h. The morphology of the clinoptilolite surface before and after modification with poly [8-oxyquinoline methacrylate] was examined by scanning electron microscopy using an electron microscope "SEM LEO 1430 VP" (Carl Zeiss, Germany).

The sorption characteristics of the synthesized material relative to the selected ions were investigated in a static mode. 0.1 g of the composite was contacted with 25–100 ml of working solutions of nitrates of the corresponding metals. The interaction took place for 10, 20, 40, 60, 120 minutes and one day with continuous mechanical shaking. Equilibrium concentrations of metal ions were recorded by the atomic absorption method.

For research of sorption properties of modified minerals, working solutions of nitrates of selected metals were prepared from sets of "Standard samples of solutions" of these salts (produced by FHI named after A.V. Bogatsky, Odesa) on the background of 1 M  $\text{HNO}_3$  with concentrations of 1 and 10 mg/ml without adding any buffer solutions.

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

$$R = (m_{\text{sorb}} / m_o) \cdot 100\% = \\ = (m_o - [m]) / m_o \cdot 100\%,$$

where  $m_o$  is the mass of the metal in the initial solution;  $m_{\text{sorb}}$  is the mass of the sorbed metal;  $[m]$  is the mass of the 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  $V$  is the volume of the equilibrium solution.

The equilibrium concentration of ions of the corresponding metals was determined by the atomic absorption method. Atomic absorption measurements were performed using a flame atomic absorption spectrophotometer "Saturn" (Ukraine) in a flame of an air-propane-butane mixture. The wavelengths of the measurements were: for copper — 324.7 nm, lead — 283.3 nm, iron — 248.3 nm, manganese — 280.1 nm, and the slit width was 0.5 cm. Calculations of equilibrium concentrations in the solution were performed by comparing the intensities of their lines in the spectrum with the lines of standard solutions. For this pur-

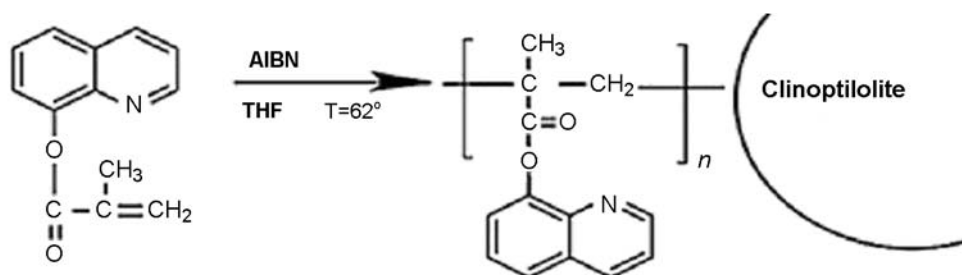


Fig. 1. Scheme of the polymerization reaction of 8-oxyquinoline methacrylate on the surface of clinoptilolite.

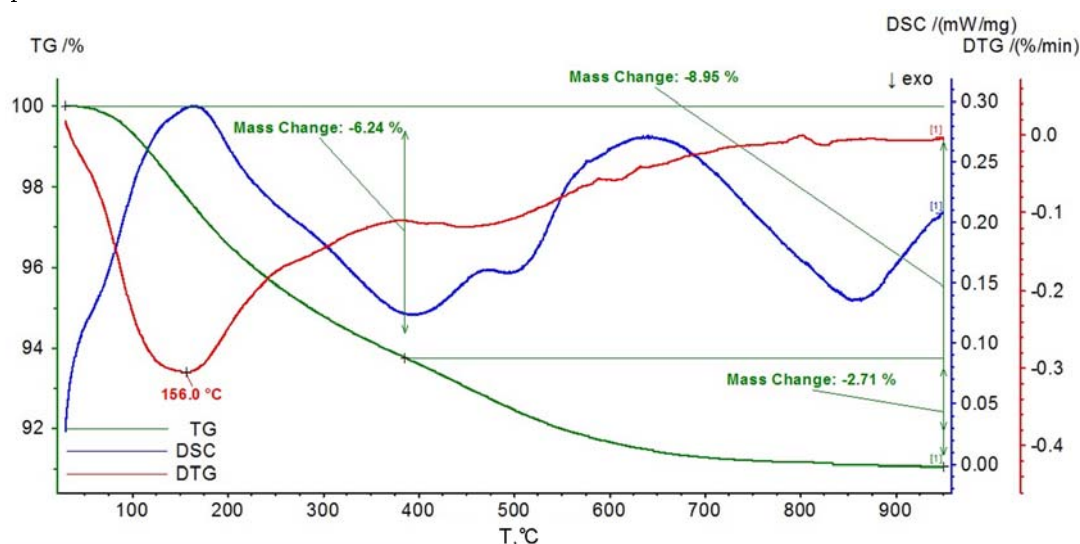


Fig. 2. Thermogram of the original clinoptilolite.

pose, standard solutions with metal concentrations of 0.1–1.5  $\mu\text{g}/\text{ml}$  were prepared.

### 3. Results and discussion

Fig. 1 shows the scheme of *in situ* polymerization of 8-oxyquinoline methacrylate on the surface of the mineral.

#### 3.1. Evidence of *in situ* immobilization of poly [8-oxyquinoline methacrylate] on the surface of clinoptilolite.

The fact of immobilization of poly [8-oxyquinoline methacrylate] on the surface of clinoptilolite was confirmed by comparative analysis of the IR spectra of the original and polymer-modified mineral. Comparative analysis of the IR spectra of the synthesized composite and the original clinoptilolite shows that in the spectra of the composite, in contrast to the original mineral, a number of new absorption bands are observed. The most informative bands for confirming the presence of poly [8-oxyquinoline methacrylate] in the surface layer of the selected mineral are a number of bands in the range of 1200–1700  $\text{cm}^{-1}$ ; these can be interpreted as follows:

— oscillations at 1590  $\text{cm}^{-1}$  correspond to the valence oscillations of CN bonds;

— absorption bands at 1750 and 1758  $\text{cm}^{-1}$  can be attributed to the valence oscillations  $\nu$  (Ar-COO-R);

— absorption bands in the range from 1394 to 1503  $\text{cm}^{-1}$  correspond to skeletal oscillations of CC bonds of the aromatic system of quinoline [14].

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 its composition.

#### 3.2. Analysis of thermal destruction of the synthesized composite using data from thermogravimetric analysis and thermographic analysis with mass spectrometry

In order to determine the mass fraction of adsorbed polymer in the composite, the thermogravimetric analysis of the synthesized composite and the source mineral was carried out (Fig. 2 and 3). As follows from the data of Fig. 3, the most intense thermal destruction of the composite occurs in the temperature range from 120 to 370°C. At the same time 11.07 % of its weight are

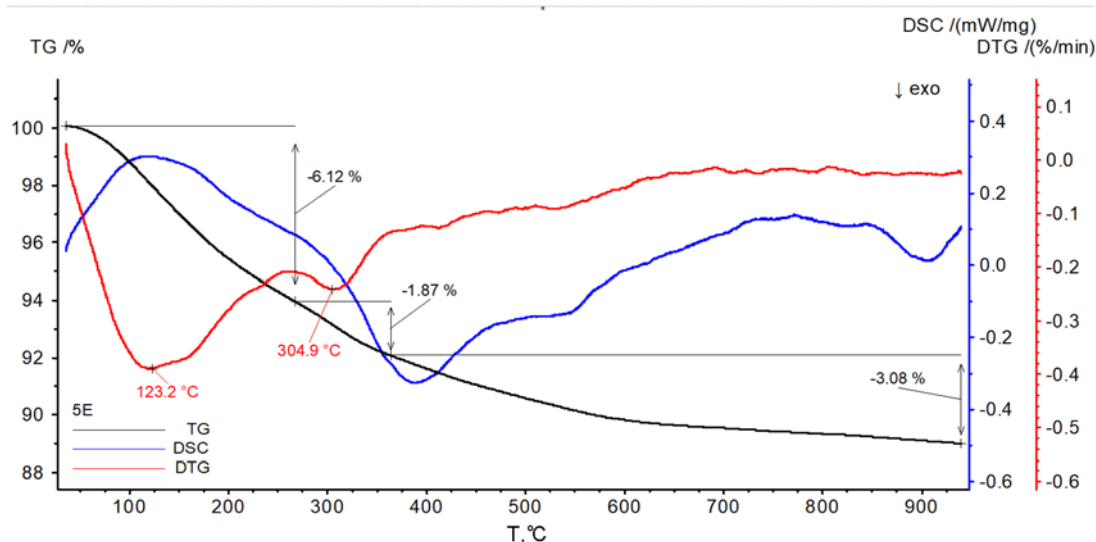


Fig. 3. Thermogram of a composite based on clinoptilolite.

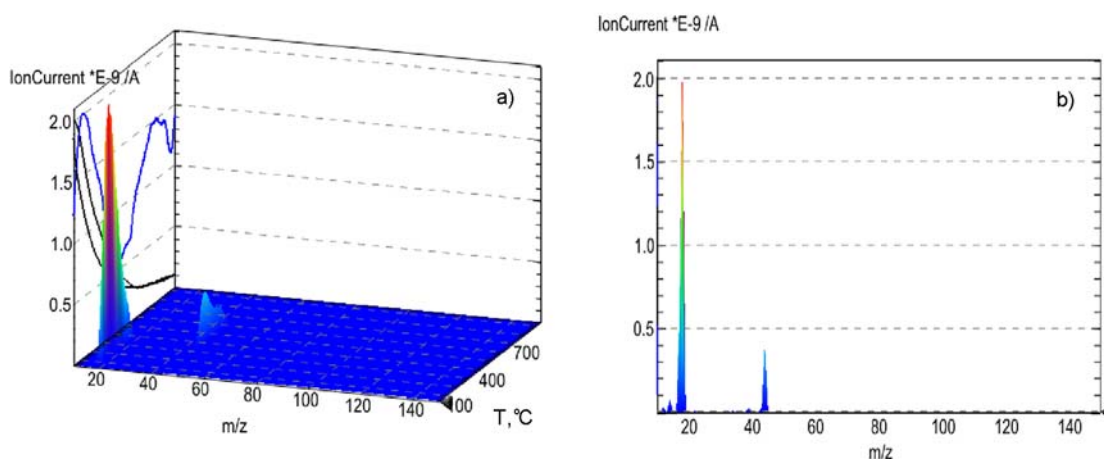


Fig. 4. a) — thermogram of the synthesized composite, combined with the mass spectrum, in 3D format; b) — the mass spectrum of the synthesized composite in 2D format.

lost. The weight loss of the source mineral vs, respectively, 8.95 % in this temperature range (see Fig. 2). Therefore, the weight of the immobilized polymer is 2.12 % in the composite. In order to detail the process of thermodestruction of a composite based on clinoptilolite, its thermogram was obtained, which is combined with the mass spectrum in 3D format (Fig. 4a) and a number of mass spectra in 2D format at different temperatures. An example of one of the spectra is shown in Fig. 4b. Analysis of the obtained mass spectra shows that the thermal destruction of the immobilized polymer occurs with the formation of two main compounds causing the most intense mass peaks (see Fig. 4b): one of them at a mass of 18 corresponds to the formation of water; the other at a mass of 44 corresponds to the release of carbon dioxide.

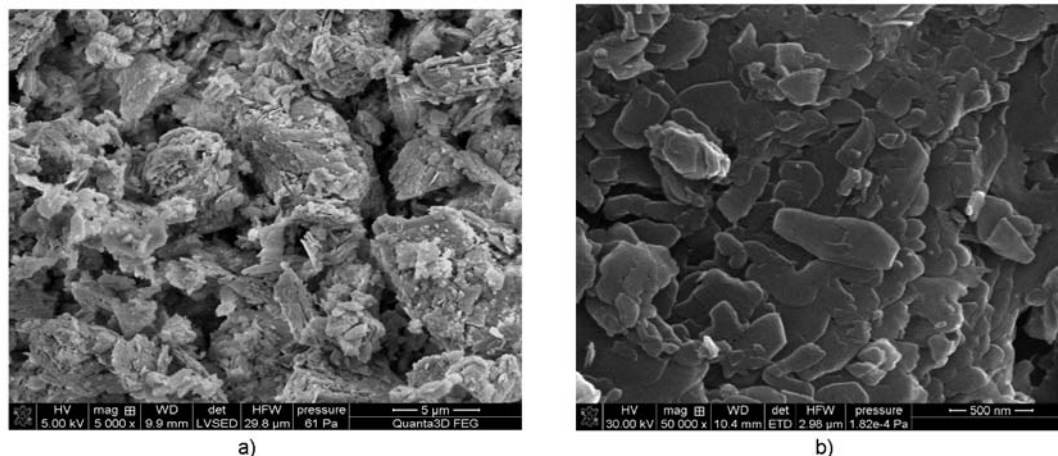
### 3.3. Comparison of clinoptilolite surface morphology before and after immobilization of poly [8-oxyquinoline methacrylate]

The method of low-temperature nitrogen adsorption-desorption was used to study the surface parameters of clinoptilolite before and after *in situ* immobilization of poly [8-oxyquinoline methacrylate]. A comparison of nitrogen adsorption-desorption isotherms obtained for the synthesized composite based on clinoptilolite and the source mineral shows that these isotherms are similar and belong to type IV isotherms according to the IUPAC classification [15]. The similarity of the nitrogen adsorption-desorption isotherms indicates that the surface structure of clinoptilolite does not change as a whole as a result of fixing the homopolymer.

The values of the surface area, average volume and pore size of the synthesized composite were calculated by different methods

Table 1. Comparative characteristics of the surface parameters of the original and *in situ* modified poly [8-oxyquinoline methacrylate] clinoptilolite

Sample	Surface area, m <sup>2</sup> /g			Average pore volume, cm <sup>3</sup> /g (BJH)	Average pore size, nm (BJH)
	<i>P/P</i> <sub>0</sub>	BET	Langmuir		
Original clinoptilolite	13.21	22.61	13.64	0.044	13.41
Composite based on clinoptilolite	3.89	3.95	5.01	0.029	29.06

Fig. 5. SEM image of the surface of the original (a) and *in situ* modified poly [8-oxyquinoline methacrylate] (b) clinoptilolite.

from the nitrogen adsorption-desorption isotherms using computer processing; the results are shown in Table 1. From Table 1, it follows that as a result of the immobilization of [8-oxyquinoline methacrylate] on the surface of clinoptilolite:

- the specific surface area decreases 5.7 times;
- the average pore volume decreases 1.5 times;
- the average pore diameter increases 2.2 times.

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

Changes in the surface morphology of clinoptilolite after *in situ* polymer modification were observed by scanning electron microscopy. SEM photos of the surface of the original and modified clinoptilolite are shown in Fig. 5. As can be seen from the photos, the polymer covers the porous surface of the mineral with a thin layer, without changing its surface structure, but only reducing its porosity, which agrees well with Table 1.

#### 3.4. Sorption properties of clinoptilolite, *in situ* modified poly [8-oxyquinoline methacrylate], relative to ions Cu<sup>2+</sup>, Pb<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>3+</sup>.

Since the synthesized composite contains quinoline groups, they should exhibit complexing activity due to the nitrogen atoms of the immobilized polymer. To confirm these considerations, we investigated the sorption of transition metal ions, which have a high affinity for nitrogen-containing ligands. Studies of the sorption capacity of the synthesized composite relative to these metal ions included:

- determination of the sorption capacity of composites for each of the studied metal ions and comparison of these values with those for the source minerals;
- study of the rate of sorption of selected ions from aqueous solutions of nitrates on the surface of the synthesized composites in a static mode;
- construction of the isotherm of sorption of each of the studied metal ions from aqueous solutions of nitrates on the surface of the synthesized composites;
- establishing the sorption capacity of the composites for each of the studied metal ions and comparison of these values with the values for the source minerals.

It was found experimentally that the time of optimal sorption of Cu(II) and Pb(II) ions on the surface of a clinoptilolite-based composite in a static mode is 1 h, and for Fe(III) and Mn(II) ions — 2 h. The established optimal time of contact of all metal ions with the composite surface was taken into account during experiments on the construction of sorption isotherms.

In order to establish the sorption capacity of the composite with respect to the selected transition metal ions, their sorption isotherms were constructed. All the obtained isotherms allowed us to unambiguously establish the sorption capacity of the original and *in situ* modified poly [8-oxyquinoline methacrylate] clinoptilolite with respect to the selected ions. The values of the sorption capacity of the source mineral and the synthesized composite with respect to the ions Pb(II), Fe(III), Cu(II) and Mn(II), which calculated from the sorption isotherms, are presented in Table 2.

As follows from Table 2, the sorption capacity of clinoptilolite after *in situ* modification of poly [8-oxyquinoline methacrylate] increases with respect to Cu(II) ions by 7.4 times, with respect to Pb(II) ions by 2.4 times with respect to Fe(III) ions by 1.4 times. For Mn(II) ions, no increase in sorption capacity was recorded. The obtained results can be explained by additional sorption as a result of complexation processes of metal ions with poly [8-oxyquinoline methacrylate] molecules, as it correlate well with the stability constants of these ions with 8-oxyquinoline.

#### 4. Conclusions

A new organo-mineral composite material was obtained by *in situ* immobilization of poly [8-oxyquinoline methacrylate] on the surface of Transcarpathian clinoptilolite (Ukraine). The fact of immobilization of the polymer on the surface of the selected inorganic matrix was confirmed by IR spectroscopy and thermogravimetric analysis combined with mass spectrometry. According to the results of thermogravimetric analysis, it was found that the mass fraction of immobilized homopolymer in the composite is 2.12 %.

Analysis of SEM images of the synthesized composite showed that the immobilized polymer on the surface of the mineral is in the form of convex agglomerates, not changing the structure of its surface, but only reducing its porosity. It was found that in the static mode, the time of optimal

Table 2. Sorption capacity of the original and *in situ* modified poly [8-oxyquinoline methacrylate] clinoptilolite

Cations	Sorption capacity, mmol/g	
	Original clinoptilolite	Composite based on clinoptilolite, <i>in situ</i> modified poly [8-oxyquinoline methacrylate]
Cu <sup>2+</sup>	0.009	0.067
Fe <sup>3+</sup>	0.0076	0.011
Pb <sup>2+</sup>	0.010	0.024

sorption of Cu(II) and Pb(II) ions on the surface of a composite based on clinoptilolite is 1 h, and Fe(III) and Mn(II) ions — 2 h. According to the results of processing of sorption isotherms, it was found that the sorption capacity of the synthesized composite with respect to the studied metal ions in comparison with the original mineral increases with respect to Cu(II) ions 7.4 times, with respect to Pb(II) ions 2.4 times, for Fe(III) ions — 1.4 times.

#### References

1. E.Plotnikov, I.Martemianova, D.Martemianov et al., *Procedia Chem.*, **15**, 219 (2015).
2. Yu.Tarasevich, *Natural Sorbents in Water Purification Processes*, Naukova Dumka, Kyiv (1981).
3. M.Fonseca, M.Oliveira, L.Aarakaki et al., *J. Colloid Interface Sci.*, **285**, 50 (2005).
4. E.Yanovska, I.Savchenko, D.Sternik et al., *Nanoscale Res. Lett.*, **12**, 313 (2017).
5. K.Ryabchenko, E.Yanovska, M.Melnyk et al., *Mater. Sci.*, **22**, 249 (2016).
6. M.K.Uddin, *Chem. Eng. J.*, **308**, 438 (2017).
7. Sh.Gu, X.Kang, L.Wang et al., *Environ. Chem. Lett.*, **17**, 629 (2019).
8. K.Ryabchenko, E.Yanovska, V.Tertykh et al., *Adsorpt. Sci. Technol.*, **32**, 88 (2014).
9. T.Budnyak, E.Yanovska, V.Tertykh et al., *Vopr. Chim. Chim. Technol.*, **5**, 43 (2010).
10. T.Budnyak, E.Yanovska, V.Tertykh et al., *Dopov. NAS Ukraine*, **3**, 141 (2011).
11. E.Yanovska, I.Savchenko, Y.Polonska et al., *Ukr. Chim. J.*, **84**, 67 (2018).
12. E.Yanovska, I.Savchenko, Y.Polonska et al., *New Mater., Comp. and Appl.*, **1**, 45 (2017).
13. I.Savchenko, E.Yanovska, Y.Polonska et al., *Nanooptics and Photonics, Nanochemistry and Nanobiotechnology, and Their Applications*. Springer Proc. Phys., 247, Chapter 5, 61 (2020)
14. A.Smiht, *Applied IR spectroscopy*, Mir, Moscow (1982) [in Russian].

15. G.D.Parfitt, C.H.Rochester, Adsorption from Solution at the Solid/Liquid Interface, Mir, Moscow (1986) [in Russian].