



Sorption properties of porous aluminosilicate minerals of Ukraine, in situ modified by poly[5-(*p*-nitrophenylazo)-8-methacryloxyquinoline] of toxic metal ions

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Abstract

The new polymer–mineral composite materials have been obtained by in situ immobilization of poly-[5-(*p*-nitrophenylazo)-8-methacryloxyquinoline] on the saponite of Tashkivsky deposit (Sap-AzoQN) and clinoptilolite of the Tushinsky deposit (Clin-AzoQN) surface. The fact of polymer immobilization on the surface of minerals by the selected method was confirmed by thermogravimetric analysis combined with mass spectrometry and IR spectroscopy. Scanning electron microscopy showed that the immobilized polymer is located on the surface of both minerals in the form of needles, located in different directions to the surface, and acicular formations. The properties of the composite materials have been determined by means of a sorption test when removing ions Pb^{2+} , Fe^{3+} , and Cu^{2+} from the model solutions in static conditions. A twofold increase in the sorption capacity of the Sap-AzoQN composite for Cu(II) and Pb(II) ions and a 5.6-fold increase in the Clin-AzoQN composite for Fe(III) ions were recorded compared to the original minerals. As a result, composite materials revealed high-efficiency sorption of heavy metals.

Keywords Adsorption · Saponite clay · Clinoptilolite · Poly-[5-(*p*-nitrophenylazo)-8-methacryloxyquinoline] · Composite · Wastewater · Cu(II) · Pb(II) · Fe(III) ions

Abbreviations

TGF Tetrahydrofuran
AIBN Azobisisobutyronitrile
IR Infrared spectroscopy

Introduction

The constant increase in the volume of polluted natural and wastewater due to anthropogenic influence requires the search for new safe methods of their treatment. Existing chemical and physico-chemical methods of cleaning polluted water (chlorination, ozonation, osmosis, etc.),

consisting of active chemical action or physical impact on water, allow removing pollutants from it. As a result, the physicochemical properties of water deteriorate and the natural balance of salts dissolved in it is disturbed. The combination of these factors has already begun to significantly affect the state of local water ecosystems and the Earth's hydrosphere as a whole.

At the same time, in nature, there are safe methods of water purification with equalization of the salt balance in it when water passes through surface and underground horizons of minerals that have great adsorption properties for anthropogenic toxic substances (clays, aluminosilicates, zeolites, etc.) (Arif et al. 2021; Bradl 2005; Chakraborty et al. 2022; Crini and Badot 2010; Jaishankar et al 2014; Li et al. 2009; Fernandes de Magalhães et al. 2022; Otunola and Ololade 2020; Yang et al. 2010; Yua and Han 2015). Such a mechanism worked and ensured a balance between the planet's geospheres throughout their existence. Accordingly, its reasonable use should form the basis of the most modern water purification technologies. The addition of such natural mineral adsorbents during the purification of wastewater and polluted natural waters at the settling stage not only allows getting rid of dangerous anthropogenic pollutants by

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adsorption without adding chemical reagents, but also to improve structure and mineralization of water (MgBemere et al. 2017).

As ecologically safe industrial adsorbent cleaners, it is promising to use such natural aluminosilicate minerals of Ukraine as saponite (saponite clay), the largest deposits of which are located in the Khmelnytskyi region of Ukraine, Transcarpathian clinoptilolites of the Sokyrnytskyi and Tushinsky deposits, bentonite, vermiculite, colored clays of the Luhansk region and Crimea, which are well known for their adsorption properties for a number of toxic organic compounds, toxic metal ions, pathogenic bacteria, etc. (Han et al. 2019; Kashif Uddin 2017; Morozova et al. 2017; Rashed and Palanisamy 2018; Srinivasan 2011; Yoldi et al. 2019).

But their natural properties can be improved, in particular, by attaching homo- or copolymers of different chemical nature to their surface, which are able to participate in the processes of ion exchange or complexation, as a result of which composite materials with valuable sorption properties are obtained.

The main methods of fixing polymers on the surface of inorganic carriers are physical and chemical fixation, sol–gel method, and in situ immobilization. Each of these methods has its advantages and disadvantages.

Grafting onto the surface of porous inorganic matrices of polyelectrolytes with a quaternary nitrogen atom in the side chain (polycations) or in the main chain (polyionenes) makes it possible to obtain effective adsorbents with ion-exchange properties for anionic forms of such anthropogenic inorganic pollutants, such as acid residues of mineral acids (in particular, nitrates, phosphates, arsenates) or oxoanions of multivalent metals (vanadates, tungstates, chromates, molybdates, and their polyanions) (Tertykh et al. 2008). In the work of Budnyak et al. (2010, 2011) and Yanovska (2015),

we reported that in situ immobilization with polyaniline on the surface of saponite from the Tashkiv deposit (Khmelnytskyi region, Ukraine) and clinoptilolite from the Sokyrnytsky deposit (Transcarpathia, Ukraine) leads to an increase in the sorption capacity of these minerals for phosphate and arsenate ions in 2–3 times in a neutral water environment.

Immobilization of polymers with oxygen-containing, nitrogen-containing, and sulfur-containing groups in the main chain, which can act as ligands, allows obtaining sorbents with complexing properties that effectively remove cations of transition toxic metals from wastewater

(Fang et al. 2007; Polonska et al. 2018; Yanovska et al. 2017, 2019; Zhang et al. 2020).

In Yanovska et al. (2020), we have shown that the sorption capacity of saponite after in situ immobilization of its surface with poly[4-methacryloyloxy-(4'-carboxy-2'-nitro)-5-methyl]-azobenzene] with respect to Cu(II) ions increases by more than 2 times, but in relation to Pb(II) and Fe(III) ions—by 15% only. And after in situ modification and adsorption on the surface of this mineral poly(8-oxyquinoline methacrylate), the sorption capacity of both composites becomes higher than the sorption capacity of the original saponite with respect to Cu(II) ions—by more than 4 times, with respect to Fe(III) ions—by almost 2 times (Yanovska et al. 2021).

Adsorption and in situ modification of poly-(8-oxyquinoline methacrylate) on the clinoptilolite surface of the Tushinsky deposit (Transcarpathia, Ukraine) increase the sorption capacity of this mineral for Cu(II), Pb(II), and Fe(III) ions (Savchenko et al. 2021).

This work is dedicated to the in situ modification of the saponite surface of the Tashkiv deposit (Khmelnytskyi region, Ukraine) and the clinoptilolite of the Tushinsky deposit (Transcarpathia, Ukraine) with a polymer whose structural link simultaneously contains an azo group, an oxyquinoline fragment, a nitro group, and poly-5-(4-nitro)phenylazo-8-methacryloxyquinoline, the study of changes in the surface structure of minerals and their adsorption properties in relation to Pb(II), Cu(II), and Fe(III) ions as a result of immobilization of this polymer.

Experimental methods

Materials and methods

Saponite from the Tashkiv deposit in the Khmelnytsky region and clinoptilolite from the Tushinsky deposit (Ukraine) were used as a mineral porous base for polymer modification. The chemical composition and the physical and chemical properties of these minerals are described in Petrenko et al. (2020).

Composite syntheses

The synthesis of 5-(4-nitro)phenylazo-8-methacryloxyquinoline was carried out by the reaction of acylation with methacrylic acid chloride in the presence of triethylamine as a hydrogen chloride acceptor in tetrahydrofuran according to the following procedure:

14.7 g (0.05 mol) of the dye was dissolved in 100 ml of dry tetrahydrofuran (THF), introduced into a flat bottom flask with a volume of 250 ml, and 10.1 g (0.1 mol)

(13.9 ml) of triethylamine was added. The mixture was intensively stirred and cooled to 0 °C, gradually over 30 min, and a solution of methacrylic acid chloride (9.7 ml in 10 ml of tetrahydrofuran) was added dropwise. After that, the reaction mixture was stirred for another 3 h until the color changed from red to orange, and then left for a day. After a day, the synthesized monomer was thoroughly washed with water and left again for a day. Then it was filtered and dried. Monomer yield—12.52 g.

The fact of monomer formation was confirmed by NMR spectroscopy: ^1H NMR (DMSO): δ 7.483–7.593(*t*, 3H), 8.850–7.849 (*s*, 2H), 2.110(*s*, 3H), 3.136–2.490 (*d*, 2H), 5.85 (*s*, 1H), 6.4 (*s*, 1H).

In situ immobilization of poly-5-(4-nitro) phenylazo-8-methacryloxyquinoline on the surface of saponite and clinoptilolite was carried out by radical polymerization of 5-(4-nitro) phenylazo-8-methacryloxyquinoline using azoisobutyronitrile (AIBN) as an initiator according to the following method:

4.17 g of monomer, 12.52 g of mineral (in the mass ratio of monomer to inorganic matrix as 1:3), and 0.209 g of azoisobutyronitrile (5% by weight of monomer) were added to a 250 ml flat-bottomed flask, and 100 ml was added—pure dry tetrahydrofuran and stirred the reaction mixture using a magnetic stirrer, periodically passing argon through it. Then the mixture was heated with intensive stirring to 60–65 °C for 6 h.

The practical yield of the composite product based on saponite was 12.40 g (74.2%), and on the basis of clinoptilolite—13.39 g (80%).

The synthesized composite based on saponite will be abbreviated as Sap-AzoQN, and based on clinoptilolite as Clin-AzoQN.

Methods

The IR spectra of the original and polymer–mineral composites were recorded on an IR spectrometer "Spectrum BX" (Perkin Elmer, Germany) in the range of 500–4000 cm^{-1} in KBr tablets.

^1H (500 MHz) spectra were recorded on a Bruker 500-MHz FT-NMR spectrometer with dimethyl sulfoxide- d_6 (DMSO- d_6) and CDCl_3 as solvents and tetra-methyl silane as an internal standard.

Thermal analysis

The amount of immobilized polymer on the surface of minerals was evaluated by thermogravimetric analysis, which was carried out using a synchronous TG/DTA analyzer "Shimadzu DTG-60 H" (Shimadzu, Japan) in the temperature range 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).

Surface morphology analysis

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

Low-temperature adsorption–desorption of nitrogen

The values of the specific surface area and the average pore diameter were calculated from the isotherms of low-temperature adsorption–desorption of nitrogen using the automated Micromeritics® ASAP® 2420 surface area and porosimetry system with software (Micromeritics, USA). Before measurement, the samples were degassed at 100 °C for 24 h.

Description of adsorption processes

Properties of the obtained composite to adsorb Cu(II), Pb(II), Cd(II), and Fe(III) were studied in static mode. Working solutions of nitrates of the corresponding metals were prepared in volumetric flasks of 25 ml, 50, or 100 ml, diluting the solutions to the mark with water, and then added the required volume to flat-bottomed flasks containing 0.1 g of 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), Pb(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.

Analysis of ion concentrations

Sorption capacity (*A*) was calculated by formula (1):

$$A = (c_0 - [M])V/m \quad (1)$$

where c_0 —is concentration of the metal in the starting solution, $[M]$ —is concentration of the metal at equilibrium, V —is the volume of the starting solution, m —is the mass of the sorbent.

The equilibrium concentration of ions of the corresponding 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 of an air-propane-butane mixture. The measurement wavelengths were: for copper—324.7 nm, for lead—283.3 nm, for ferrum—248.3 nm, and the slit width

was equal to 0.5 cm. The equilibrium concentrations in the solution were calculated by comparing the intensities of their lines in the spectrum with the intensities of the lines of standard solutions. For this, standard solutions with metal concentrations of 0.1–1.5 $\mu\text{g/ml}$ were prepared.

Results and discussion

The new polymer–mineral composite materials have been synthesized by in situ polymerization of [5-(*p*-nitrophenylazo)-8-methacryloxyquinoline] on the saponite of Tashkivsky deposit (Sap-AzoQN) and clinoptilolite of the Tushinsky deposit (Clin-AzoQN) surface.

In situ modification of the surface of saponite and clinoptilolite by poly-5-(4-nitro)-phenylazo-8-methacryloxyquinoline was carried out by radical polymerization of 5-(4-nitro)-phenylazo-8-methacryloxyquinoline using AIBN as an initiator (Fig. 1).

The fact of in situ immobilization of poly-5-(4-nitro)-phenylazo-8-methacryloxyquinoline on the surfaces of saponite and clinoptilolite was confirmed by comparative analysis of

the IR spectra of the original and polymer-modified minerals. Examples of such spectra for the original clinoptilolite and the composite on its basis (Clin-AzoQN) are shown in Fig. 2a, b.

As can be seen from Fig. 2b, the most informative for confirming the presence of poly-5-(4-nitro)phenylazo-8-methacryloxyquinoline in the surface layer of clinoptilolite is the region of the spectrum from 1200 to 1800 cm^{-1} , the absorption bands of which can be interpreted as follows:

- vibrations at 1280 cm^{-1} and 1300 cm^{-1} correspond to stretching and deformation vibrations of C–H bonds;
- absorption bands in the interval from 1394 to 1503 cm^{-1} correspond to skeletal vibrations of C–C bonds of the quinoline aromatic system;
- stretching vibrations $\nu(\text{C–N})$ are observed at 1590 cm^{-1} ;
- absorption band at 1650 cm^{-1} —to asymmetric vibrations of NO_2 -groups;
- the absorption band at 1760 cm^{-1} —to the stretching vibrations of COO-groups.

The presence of these absorption bands in the IR spectra of the obtained composites may indicate the presence of

Fig. 1 Scheme of the polymerization reaction of 5-(4-nitro)-phenylazo-8-oxyquinoline during in situ immobilization of poly-5-(4-nitro)-phenylazo-8-methacryloxyquinoline on the surface of saponite and clinoptilolite

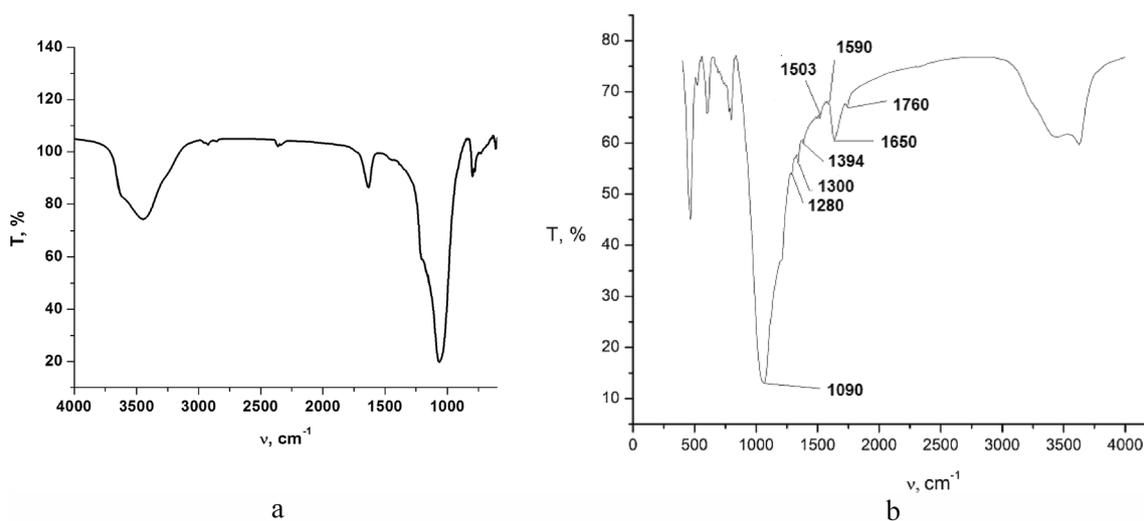
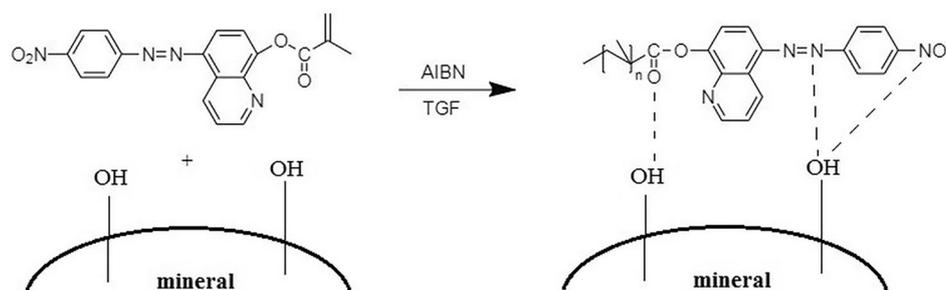


Fig. 2 IR spectra of the original clinoptilolite (a) and the composite Clin-AzoQN (b)

poly-5-(4-nitro) phenylazo-8-methacryloxyquinoline in their composition.

Thermograms of the original minerals and the composites on their basis are shown in Figs. 3, 4, 5, and 6, respectively. As a result of the comparison of thermograms (Figs. 3, 4),

it can be stated that the total mass loss for the synthesized Sap-AzoQN composite is 13.95%, while for the original saponite, it is 10.50%.

Therefore, the mass fraction of in situ immobilized polymer in the synthesized composite is 3.45%. According to the

Fig. 3 Thermogram of the original saponite

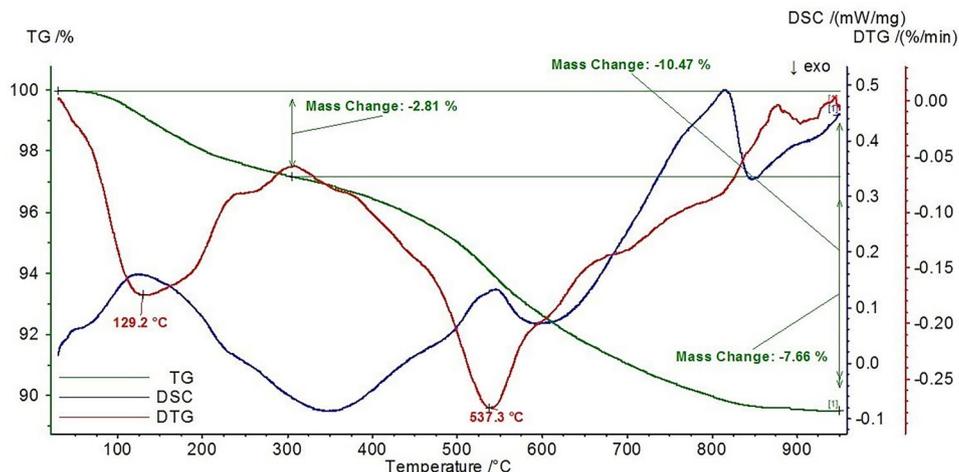


Fig. 4 Thermogram of the synthesized Sap-AzoQN composite

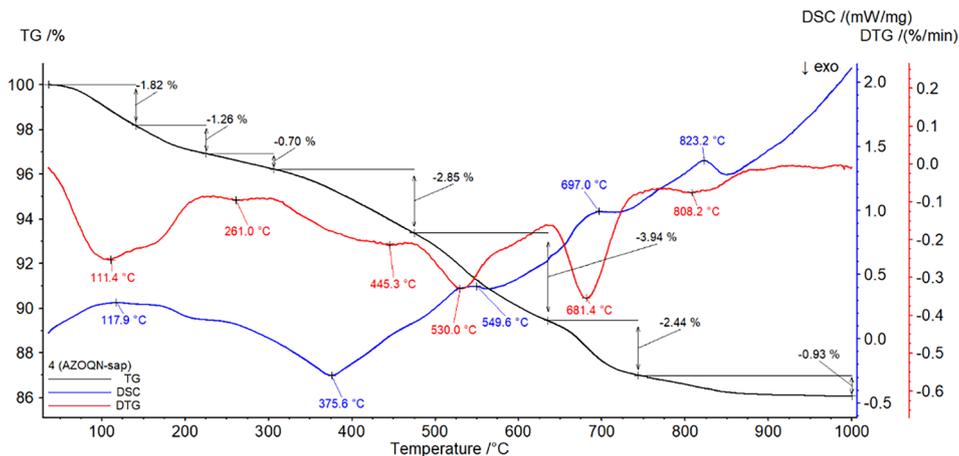


Fig. 5 Thermogram of the original clinoptilolite

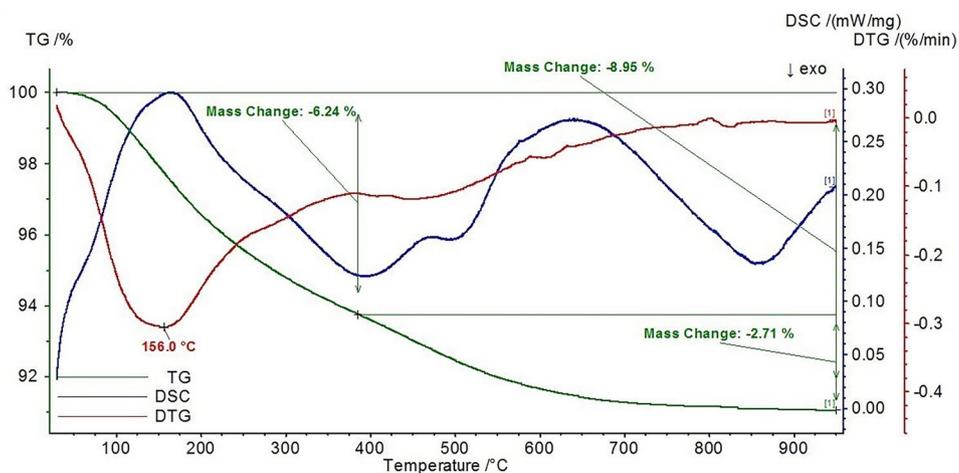
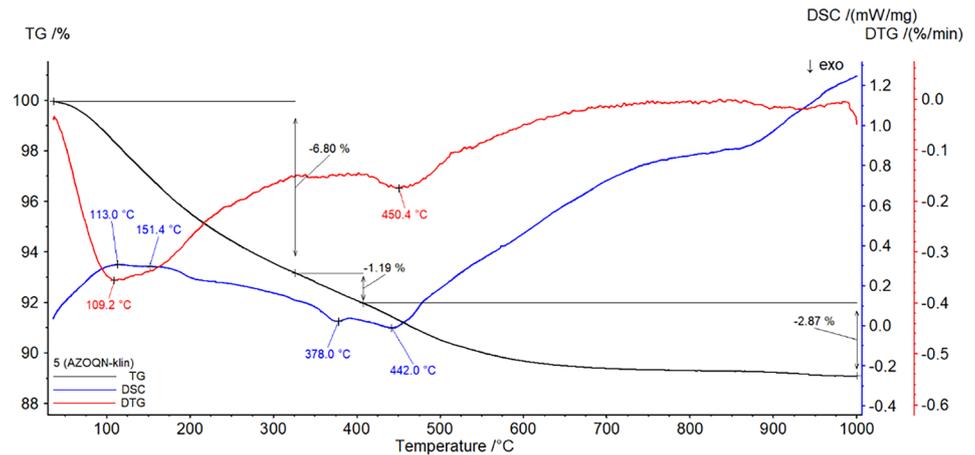


Fig. 6 Thermogram of the synthesized Clin-AzoQN composite



thermograms (Figs. 5, 6), the total mass loss for the Clin-AzoQN composite is 10.90%, and for the original clinoptilolite—8.95%. Therefore, the mass fraction of the in situ immobilized polymer in the Clin-AzoQN composite is about 2.00%.

In order to establish the products of thermal degradation of immobilized poly-5-(4-nitro)phenylazo-8-methacryloxyquinoline on the surface of saponite and clinoptilolite, thermograms of the polymer–mineral composites combined with mass spectra were obtained in 3D format (Figs. 7, 8) and a number of their mass spectra at different temperatures in 2D format.

As can be seen from Fig. 7 and as follows from the analysis of the obtained mass spectra of the Sap-AzoQN composite, the final thermal destruction of the immobilized polymer on the saponite surface occurs mainly with the formation of water (mass peak at 18) and carbon dioxide (mass peak at 44) with small impurities of nitrogen

and (or) carbon(II) oxide (mass peak at 28), ethane (mass peak at 30).

As follows from Fig. 8 and the analysis of the obtained mass spectra of the Clin-AzoQN composite, the quantitative composition of the thermal degradation products of poly-5-(4-nitro)phenylazo-8-methacryloxyquinoline, which is immobilized on the surface of clinoptilolite, is slightly different from the composition of the products for Sap-AzoQN. Thermal degradation occurs mainly with the formation of nitrogen and (or) carbon(II) oxide (mass peak at 28) and with the formation of water (mass peak at 18) with small impurities of carbon dioxide (mass peak at 44).

The method of low-temperature adsorption–desorption of nitrogen was used to study changes in mineral surface parameters after immobilization of poly-5-(4-nitro)phenylazo-8-methacryloxyquinoline.

Fig. 9 shows examples of low-temperature nitrogen adsorption–desorption isotherms of the original saponite (a) and the Sap-AzoQN composite (c). As can be seen from the

Fig. 7 TG-MS-3D (a) and MS-2D (b) of the synthesized Sap-AzoQN composite

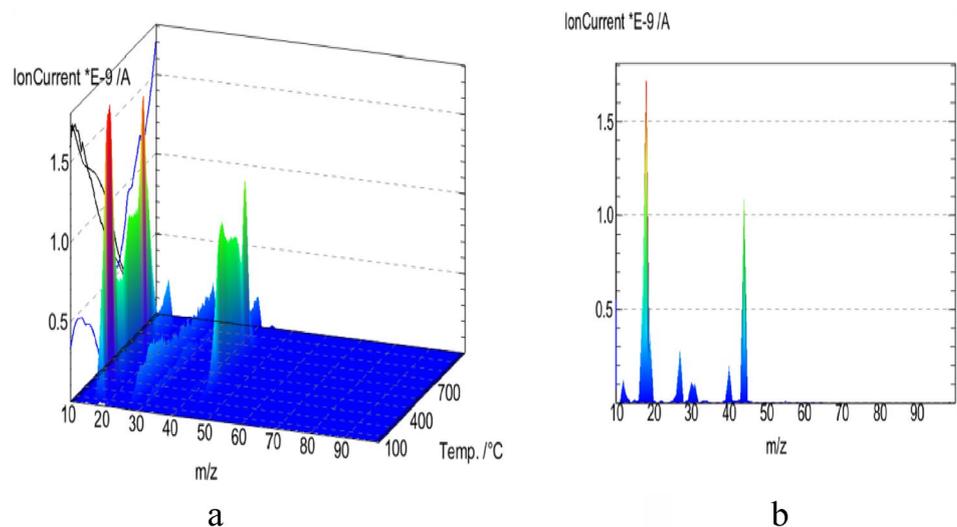
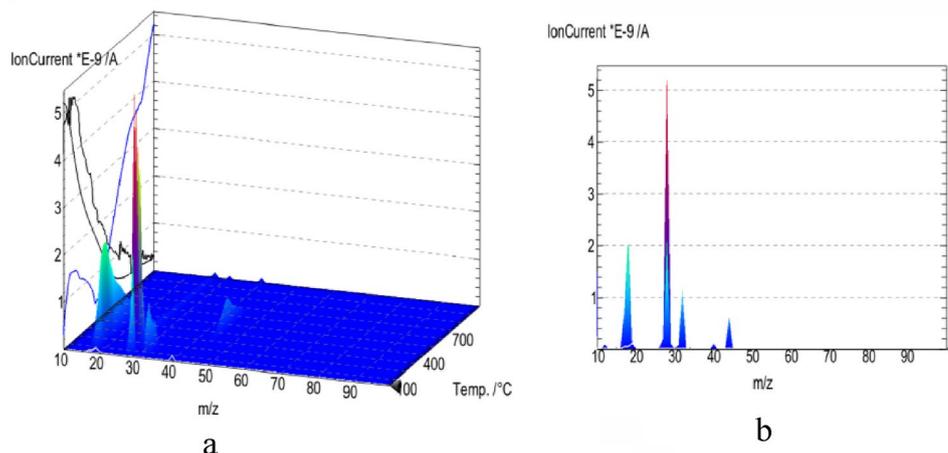


Fig. 8 TG-MS-3D (a) and MS-2D (b) of the synthesized Clin-AzoQN composite



given Fig. 9, the nitrogen adsorption–desorption isotherms of the synthesized composite and the original mineral are similar, which indicates that the surface structure of the saponite does not change as a result of fixing the polymer by the chosen method. A similar situation is observed for the composite based on clinoptilolite.

The obtained nitrogen adsorption–desorption isotherms (Figs. 9, 10) of the synthesized composites and the original minerals are similar, which indicates that the surface structure of the minerals does not change as a result of fixing the polymer by the chosen method.

By means of computer processing of the obtained nitrogen adsorption–desorption isotherms by various methods, the values of the specific surface area of the original minerals and synthesized composites were obtained and compared. Average diameter and pore volume values were found

from surface pore size distribution diagrams of the original minerals and composites calculated using the BJH method. The obtained values of the surface parameters of the original minerals and polymer–mineral composites are shown in Table 1.

After analyzing the data in Table 1, it can be stated that:

- the specific surface area of saponite after in situ immobilization of poly-5-(4-nitro)-phenylazo-8-methacryloxyquinoline decreases by approximately 4 times, and that of clinoptilolite by approximately 3 times, which is a logical result of fixation on the surface of a non-porous polymer;
- the average pore volume for the Sap-AzoQN composite decreases by 2.5 times compared to the original saponite, while for the Clin-AzoQN composite it decreases slightly

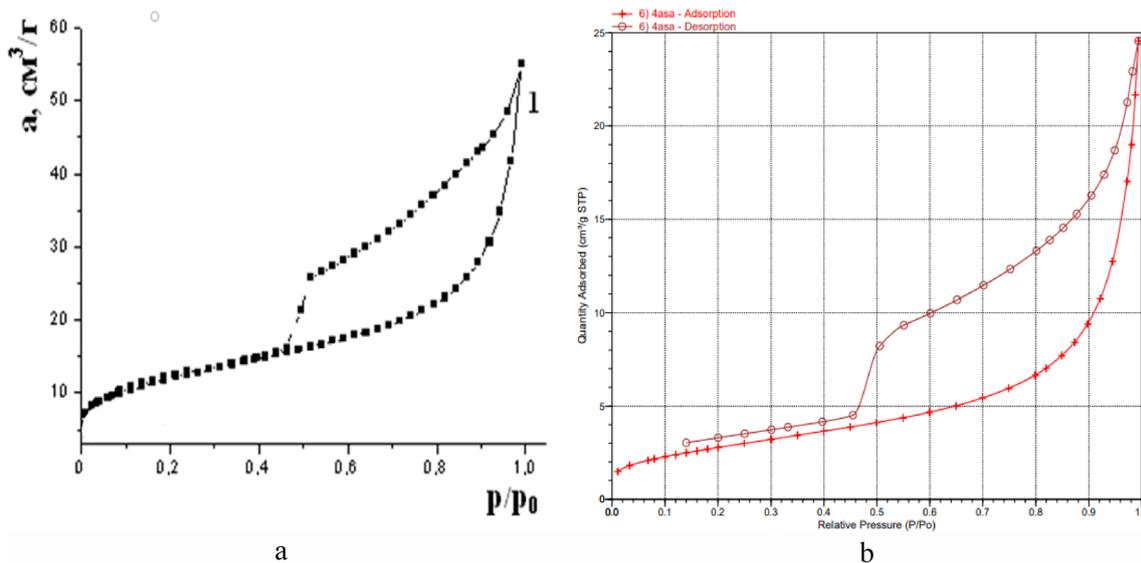


Fig. 9 Low-temperature nitrogen adsorption–desorption isotherms of the original saponite composite (a) and the Sap-AzoQN composite (b)

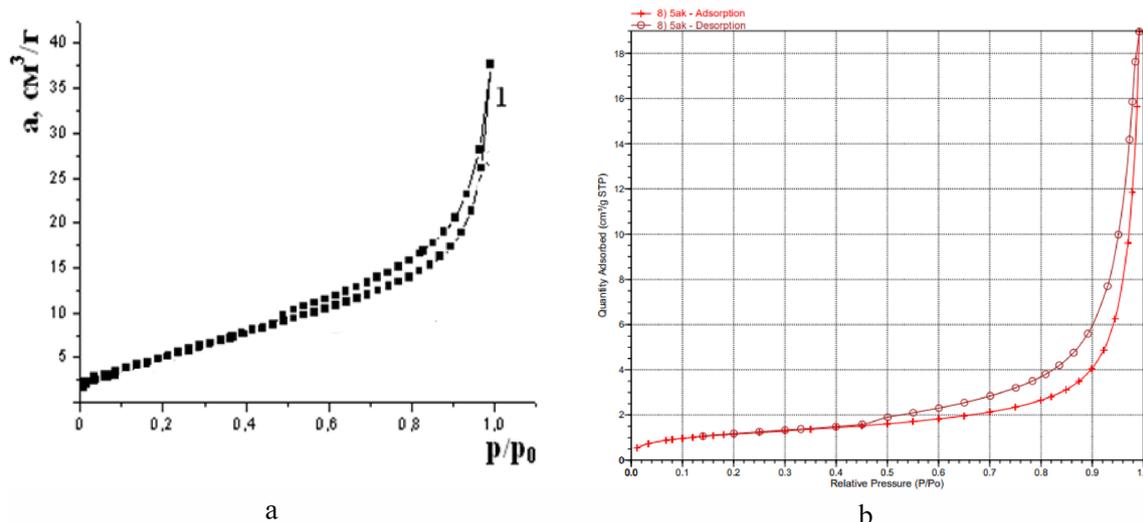


Fig. 10 Low-temperature nitrogen adsorption–desorption isotherms of the original clinoptilolite composite (a) and the Clin-AzoQN composite (b)

Table 1 Comparison of surface parameters of original minerals and synthesized composites

Sample	S_{sp} , m^2/g			Average pore volume, cm^3/g	Average pore size, nm
	According to the isotherm	BET	Langmuir		
Original saponite	41.0	41.0	65.0	0.10	8.0
Sap-AzoQN	9.8	10.3	15.5	0.04	14.8
Original clinoptilolite	13.0	13.0	14.0	0.10	14.0
Clin-AzoQN	4.0	4.2	6.2	0.03	28.3

more – by 3.3 times compared to the original clinoptilolite;

- The average pore size of the composites increases approximately 2 times compared to the original minerals.

These changes in mineral surface parameters indicate that the polymer modification only "smoothes out" the porosity of the original minerals, simultaneously reducing the depth of their pores and expanding them, which confirms the successful immobilization of the polymer on a solid surface.

Changes in the surface morphology of minerals after in situ modification with poly-5-(4-nitro)phenylazo-8-methacryloxyquinoline were monitored using scanning electron microscopy (SEM). SEM photos of the surface of the original saponite and the composite synthesized on its basis are shown in Fig. 11, and of the original clinoptilolite and the composite synthesized on its basis—in Fig. 12.

Analysis of the given photos proves that.

- in situ immobilization of poly-5-(4-nitro)phenylazo-8-methacryloxyquinoline on the surface of both minerals practically does not affect their surface structure;
- the immobilized polymer is located on the surface of both minerals in the form of needles, which are located in different directions to the surface, and acicular formations (see Fig. 11c, d). This form of arrangement of the immobilized polymer is quite successful with regard to the participation of its macromolecules in complexation processes, since the vast majority of active centers of complexation in the composition of macromolecules remain sterically accessible to metal ions.
- photos 11b and 12b demonstrate how the immobilized polymer "smoothes out" the porosity of the original minerals, and photos 11c and 11d—how it tries to expand these pores.

Thus, the results of studying the surface of the polymer–mineral composites by scanning electron microscopy and by the method of low-temperature nitrogen adsorption–desorption are in good agreement with each other.

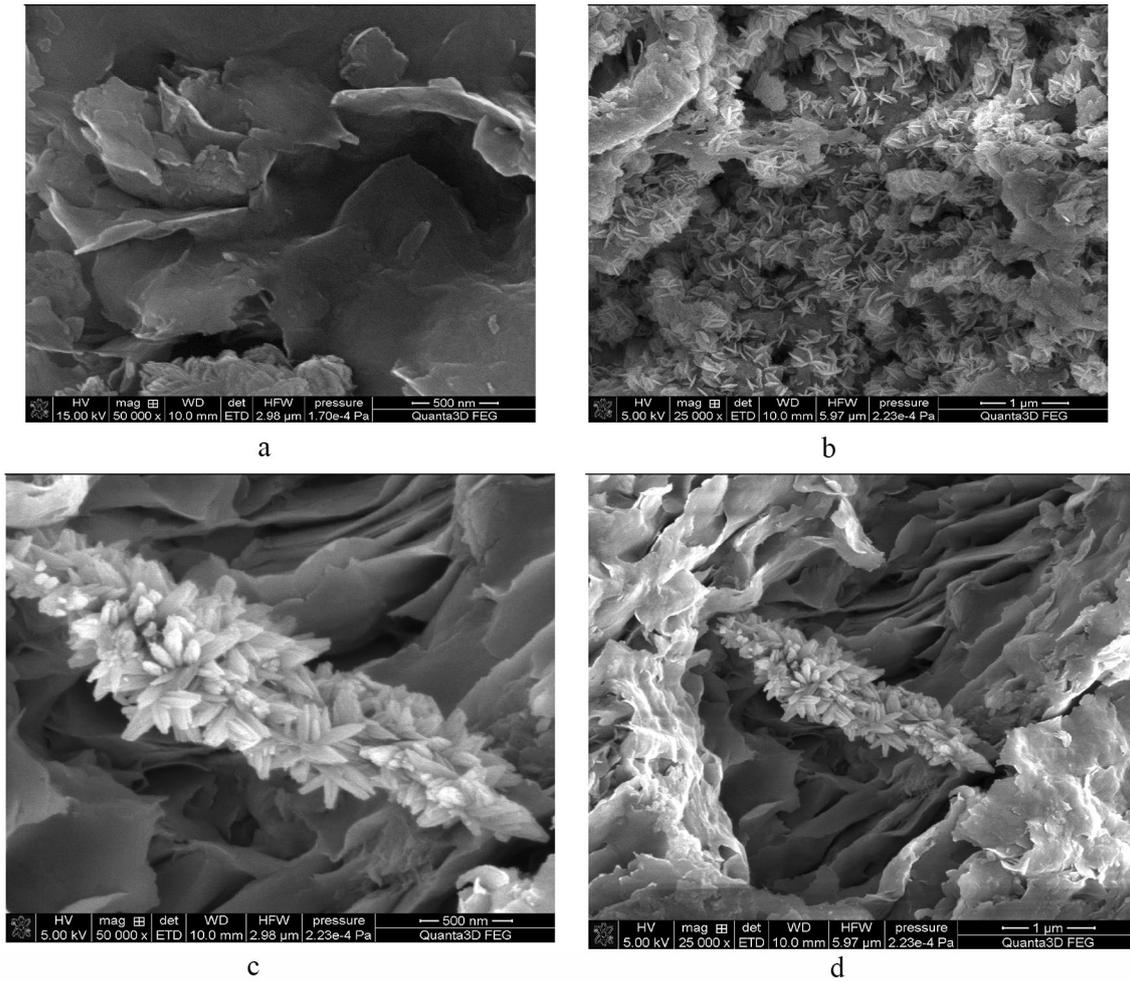


Fig. 11 SEM photo of the surface of the original saponite (a 50,000-fold magnification) and the synthesized Sap-AzoQN composite (c 50,000-fold magnification; b, d 25,000-fold magnification)

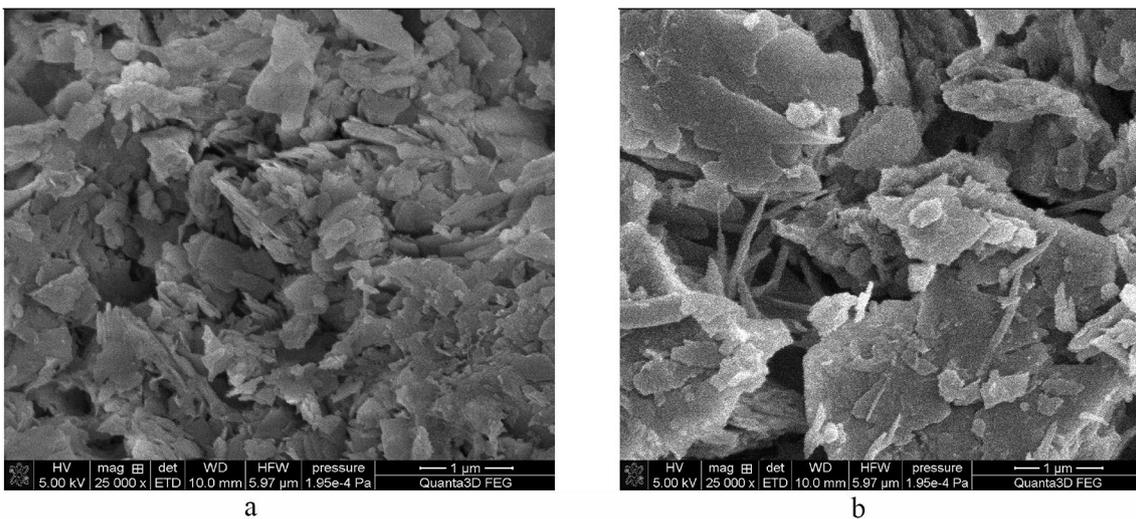


Fig. 12 SEM photo of the surface of the original clinoptilolite (a) and the synthesized Klin-AzoQN composite (b) at a magnification of 25,000 times

As can be seen from the SEM photo (Figs. 11, 12), polymer macromolecules in the form of fibers are located in the pores of the surface of minerals of different sizes, but do not completely cover them (the pores do not disappear! Neither small nor large!), as a result, the depth of the pores decreases and their slight expansion may occur.

Since the structural link of immobilized poly-5-(4-nitro)phenylazo-8-methacryloxyquinoline on the surface of natural aluminosilicate minerals of Ukraine contains an azo group, an oxyquinoline fragment, and a nitro group at the same time, the synthesized composites should show sorption activity toward transition metal ions, which form strong (stable) nitrogen-containing complexes. Due to the formation of complexes with macromolecules of the immobilized polymer on the surface of the synthesized composites, ions of these metals should be actively sorbed, and the synthesized composites should play the role of more active sorbents in comparison with the original minerals. To test these considerations, the sorption on the surface of synthesized composites of Fe(III), Pb(II), and Cu(II) ions, which are multi-ton anthropogenic pollutants of the hydrosphere and have a high affinity for nitrogen-containing ligands, was investigated.

In order to establish the values of the sorption capacity of the synthesized composites with respect to selected transition metal ions, their sorption isotherms were constructed and compared with the isotherms for the original minerals. Examples of such sorption isotherms of Pb(II) and Cu(II) ions on the surface of Sap-AzoQN are shown in Fig. 13, and the sorption isotherm of Cu(II), Pb(II), Cd(II), and Fe(III) ions on the surface of the composite Clin-AzoQN—in Fig. 14. As can be seen from these figures, all the given isotherms belong to the 2L type and allow us to unambiguously establish the value of the sorption capacity for each of the investigated ions.

Table 2 shows the results of comparing the values of the sorption capacity of the original saponite, saponite-based composites with poly(8-oxyquinoline methacrylate)

immobilized by various methods, and the Sap-AzoQN composite with respect to Cu(II), Pb(II), and Fe(III) ions.

The data in Table 2 allow us to state that the sorption capacity of saponite after in situ polymerization of 5-(4-nitro)phenylazo-8-methacryloxyquinoline in the molar ratio increases with respect to Cu(II) and Pb(II) ions by 2 times and is higher in more than 1.5 times for Pb(II) ions compared to the sorption capacity of the composite with in situ immobilized poly(8-oxyquinoline methacrylate) and more than 2.7 times higher than the sorption capacity for the composite with adsorbed poly(8-oxyquinoline methacrylate).

The data in Table 3 indicate that the sorption capacity of clinoptilolite after in situ modification with poly-5-(4-nitro)phenylazo-8-methacryloxyquinoline in the molar ratio for Cu(II) and Pb(II) ions do not change, but for Fe ions (III) increases by 5.6 times and is more than 4 times higher for these ions compared to the sorption capacity of the composite with in situ immobilized poly(8-oxyquinoline methacrylate) and 2.5 times higher than the sorption capacity for the composite with adsorbed poly(8-oxyquinoline methacrylate).

The obtained results on the increase in the sorption capacity of the saponite-based composite for Cu(II), Pb(II) ions, and the clinoptilolite-based composite for Fe(III) ions in comparison with the original minerals can be explained by the chemical nature of the immobilized polymer: the presence of the polymer structural chain of three powerful centers of coordination of the oxyquinoline group, and azo and nitro groups, as well as a rather successful form of the arrangement of the immobilized polymer on the surface of minerals, which is the result of the chosen method of fixing the polymer on the surface of porous minerals.

As follows from the comparison of Tables 2 and 3, the sorption capacity of composites with respect to metal ions of different types differs significantly. The obtained results, in our opinion, can be explained by the different concentration and different steric accessibility of the active centers

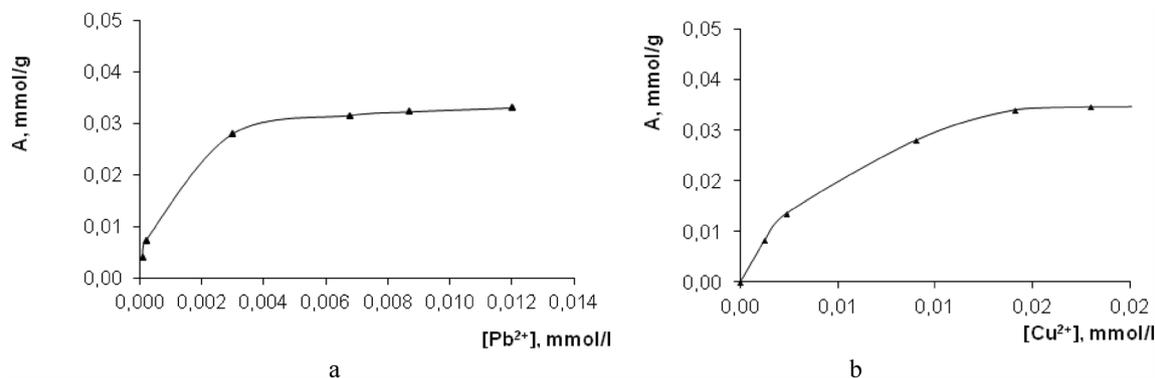


Fig. 13 Sorption isotherms of Pb(II) (a) and Cu(II) (b) ions on the Sap-AzoQN surface from aqueous nitrate solutions (without adding buffer solutions) in static mode, sorption time—1 day

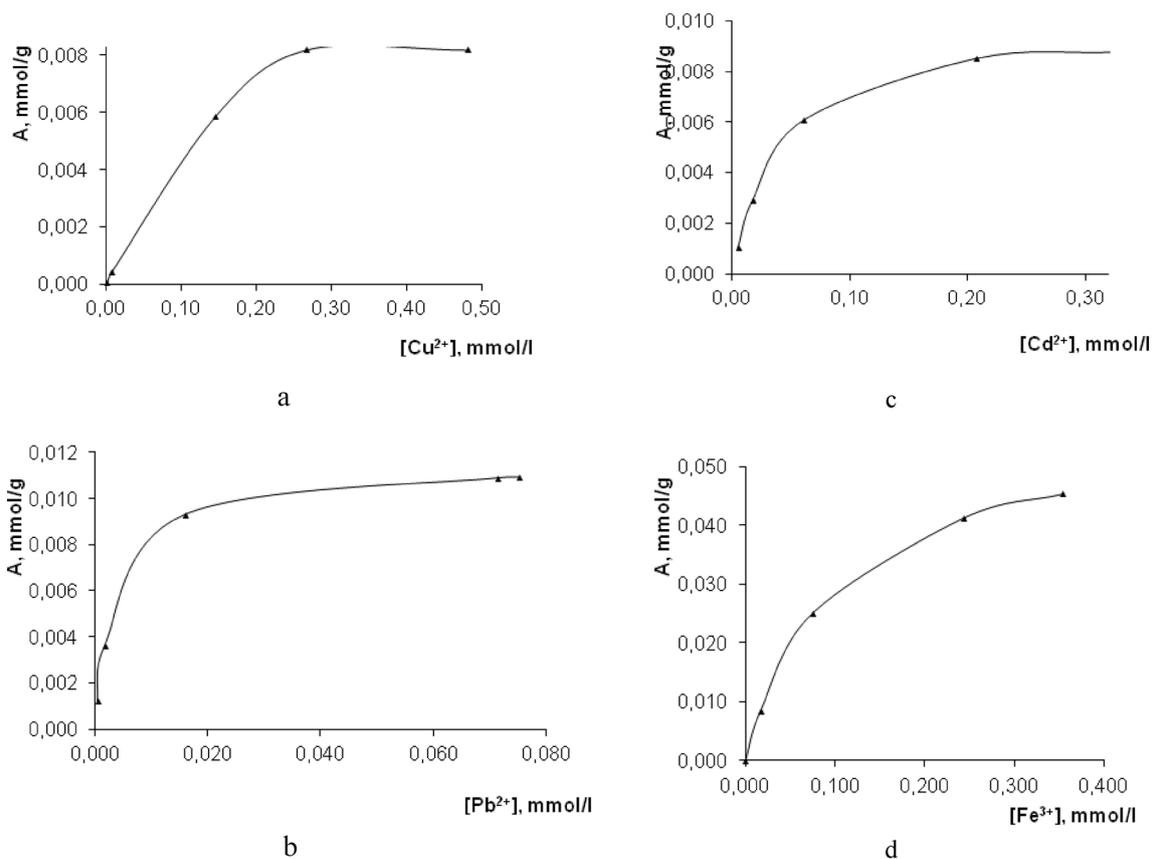


Fig. 14 Sorption isotherms of Cu(II) (a), Pb(II) (b), Cd(II) (c), and Fe(III) (d) ions on the Clin-AzoQN surface from aqueous nitrate solutions (without adding buffer solutions) in static mode, sorption time—1 day

Table 2 Comparison of the sorption capacity for Cu(II) and Pb(II) ions of the original saponite, saponite-based composites with poly(8-oxyquinoline methacrylate) immobilized by various methods, and the Sap-AzoQN composite, mmol/g

Sorbent	Cu(II)	Pb(II)
Original saponite	0.017	0.016
Saponite, in situ modified with poly(8-oxyquinoline methacrylate) (Yanovska et al. 2021)	0.064	0.021
Saponite with adsorbed poly(8-oxyquinoline methacrylate) (Yanovska et al. 2023)	0.075	0.012
Composite Sap-AzoQN	0.035	0.033

Table 3 Comparison of the sorption capacity for Cu(II), Pb(II), and Fe(III) ions of the original clinoptilolite, composites based on clinoptilolite with poly(8-oxyquinoline methacrylate) immobilized by various methods, and Clin-AzoQN composite, mmol/g

Sorbent	Cu(II)	Pb(II)	Fe(III)
Original clinoptilolite	0.009	0.01	0.008
Clinoptilolite, in situ modified with poly(8-oxyquinoline methacrylate) (Savchenko et al. 2021)	0.067	0.024	0.011
Clinoptilolite with adsorbed poly(8-oxyquinoline methacrylate) (Savchenko et al. 2021)	0.094	0.034	0.018
Composite Clin-AzoQN	0.009	0.011	0.045

of complexation, which are the immobilized polymer molecules, due to their different location on the surface of these minerals, as can be seen from the given SEM photos. First, according to thermogravimetric analysis, the concentration of immobilized polymer on the surface of saponite

is higher (3.45 wt%) than on the surface of clinoptilolite (2%). Second, on the saponite surface, there is a higher concentration of "open", sterically accessible immobilized polymer molecules (see SEM photo), so complexation processes with Cu(II) and Pb(II) ions occur more intensively.

Conclusions

Saponite from the Tashkiv deposit (Ukraine) and clinoptilolite from the Tushinsky deposit (Ukraine) has been modified by immobilization of poly-5-(4-nitro)-phenylazo-8-methacryloxyquinoline on the surface that provides extended sorption properties.

According to the results of thermogravimetric analysis, it was found that the mass of immobilized polymer in the composition of Sap-AzoQN is 3.5%, and in the composition of Clin-AzoQN—2.0%.

Changes in mineral surface parameters after in situ modification by poly-5-(4-nitro)phenylazo-8-methacryloxyquinoline, namely their specific surface area, average diameter, and pore volume, indicate that polymer modification does not affect the surface structure minerals, but only "smooths out" the porosity of the original minerals, simultaneously reducing the depth of their pores and expanding them.

It was established that the sorption capacity of saponite after in situ immobilization of poly-5-(4-nitro)phenylazo-8-methacryloxyquinoline in the molar ratio increases with respect to Cu(II) and Pb(II) ions by 2 times and the sorption capacity of clinoptilolite with respect to Cu ions(II) and Pb(II) does not change, but with respect to Fe(III) ions, it increases by 5.6 times.

This phenomenon can be explained by the chemical nature of the immobilized polymer and the successful arrangement of the immobilized polymer on the mineral surface as a result of the chosen immobilization method.

Thus, polymer–mineral composite materials as sorbents are suggested for efficient water purification under certain environmental conditions.

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Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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