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SORPTION PROPERTIES FOR IONS OF TOXIC METALS OF CARPATHIAN CLINOPTILOLITE (UKRAINE), *IN SITU* MODIFIED BY POLY[*N*-(4-CARBOXYPHENYL)METHACRYLAMIDE]

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Abstract. A new organo-mineral nanocomposite material was obtained by in situ immobilization of poly[N-(4-carboxyphenyl)methacrylamide] on the surface of Carpathian clinoptilolite (Ukraine). According to the results of TG and DSC-MS analysis, we found out that the mass of the immobilized polymer is 18%. As a result of the comparison of the sorption properties of the modified and original minerals regarding to the Pb(II), Cd(II), Cu(II), Mn(II) and Fe(III) ions, improvement was recorded after modification by the polymer selected regarding to the ions Pb(II), Cd(II) and Cu(II).

Keywords: *adsorption, in situ immobilization, clinoptilolite, poly[N-(4-carboxyphenyl)methacrylamide], composite, heavy metals.*

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1. Introduction

The presence of large volumes of scattered toxic metals in the biosphere as a result of corrosion and leaks in the production processes makes it relevant to find new technologies for their removal from contaminated water and soil in order to isolate the biosphere and re-use. Concerning this, the search for inexpensive non-toxic sorbents, which can used effectively to remove toxic ions from wastewater or contaminated natural waters, remains to be the subject of contemporary interest. For this purpose, it is advisable to use natural porous minerals, in particular zeolites and clays. Carpathian clinoptilolites belong to Ukrainian natural minerals, widely known for their sorption properties in relation to various anthropogenic substances (Galla et al., 1988; Yanovska et al., 2008). To improve the sorption properties of natural minerals, it is expedient to modify their surface with substances capable of complexation and ion exchange, such as nitrogen and oxygen-containing polymers (Budnyak et al., 2016; Ryabchenko et al., 2016; Wan Ngah et al., 2012).

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

forms an ordered layer of polymer, 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 the method usedof immobilizing polymers on solid surfaces has an advantage due toit universality with respect to the chemical nature of the carrier (Sapurina & Stejskal, 2008).

As it comes from the review of modern literary sources, 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.

In (Yanovska et al., 2017) we have shown that *in situ* immobilization of poly [*N*-(4-carboxyphenyl)methacrylamide] on the surface of silica gel allowes us to obtain a material with a sorption capability to ions Cu(II), Pb(II) and Ni(II).

This work is devoted to the modification of the clinoptilolite surface (Tushin deposit located in the Carpathian region in Ukraine) by the polymethacrylamide4-aminobenzoic acid *using in situ* heterophase polymerization and the sorption properties of the modified mineral to ions of toxic metals such as Cu(II), Pb(II), Cd(II), Mn(II) and Fe(III).

2. Experimental

Materials

Clinopotylolite of the Tushin deposit, located on the territory of the Carpathian region in Ukraine, had the following parameters: the chemical formula $Na[AlSi_5O_{12}]\cdot 6H_2O$; chemical composition (mas. %): SiO_2 – 67,07; Al_2O_3 – 12,4; K_2O – 2,8; CaO – 2,09; Na_2O – 2,05; Fe_2O_3 – 0,9; FeO – 0,76; TiO_2 – 0,19; P_2O_5 – 0,117; MgO – 0,072; MnO – 0,07; SO_3 – 0,08; porosity–45%; the average pore diameter is 50 nm, the specific surface area– 22 m^2/g.

Methods

In situ immobilization of *N*-(4-carboxyphenyl)methacrylamide on the surface of clinoptilolite was committed according to the following procedure:

4.18 g of 4-carboxyphenyl methacrylamide and 0.0836 g of azoisobutyronitrile (AIBN) (2% of monomerweight) were dissolvedin 100 ml of tetrahydrofuran (THF), placed in a heat-resistant flask and added 12.54 g of clinoptilolite while vigorous lystirring. The reaction mixture was heated to 62°C during 5 hours, under continuous mechanical stirring. After, the synthesized composite removed from the reactor, filtered off from the solution, and dried overnight.

FTIR spectra of the samples of initial composite and the derived composite were record 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 record in the spectral range of 500–4000 cm^{-1} with 16 scans per spectrum at a resolution of 4 cm^{-1}.

Thermal analysis was carried out on a STA 449 Jupiter F1, Netzsch (Germany) under the following operational conditions: heating rate of 10^oC min^{-1}, dynamic atmosphere of synthetic air (50 mL min^{-1}), temperature range of 30–950^oC, sample

mass ~18 mg, sensor thermocouple type S TG-DSC. As a reference was used empty crucible made out of Al_2O_3. 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.

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

The investigations of adsorption properties.

Properties of the obtained composite to adsorb Cu(II), Cd(II), Pb(II), Mn(II), Fe(III) were studied in static mode. Working solutions of the nitrates of corresponding metals were prepared using 25 ml, 50 or 100 ml volumetric flasks, diluting solutions to the mark with standard buffer solutions of certain pH level 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), Cd(II), Mn(II), Fe(III) are prepared with the sets of "standard sample solutions" of these salts on 1M HNO_3 background (produced by A.V. Bogatsky FHI in Odesa) with concentrations of 1 and 10 mg/ml.

To create pH level at 4.0, we used a standard phthalate buffer solution prepared from a certified reference material (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 liter volumetric flask and 5 ml of 6.5 M (25%) of ammonia solution was added. The exact pH was verified using a pH meter "HANNA TESTER WP", adding acetic acid or ammonia solution drop wise. 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 level volumeof 25 mlcontaining 100 μgof metal ion were shaken from 0.1 g of sorbent for 5-90 minutes. After sorption for 5, 10, 20, 30, 60 and 90 minutes 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.

Calculations

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

$$A = (c_o - [\mathrm{M}])\, V / m$$

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

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

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

where m_o is a mass of metal in the starting solution (μg), m_{sorp} is a mass of the sorbed metal, $[m]$ is a mass of the metal at equilibrium after the sorption, which was found

$[m] = \mathrm{C} \cdot V$, where C is a concentration of the metal at equilibrium ($\mu g/ml$) and V is the volume of the solution at equilibrium (ml).

3. Results and discussion

Physicochemical characteristics of the synthesized composite

Figure 1 shows a scheme for polymerization reaction of *N*-(4-carboxyphenyl)methacrylamide on the surface of clinoptilolite.

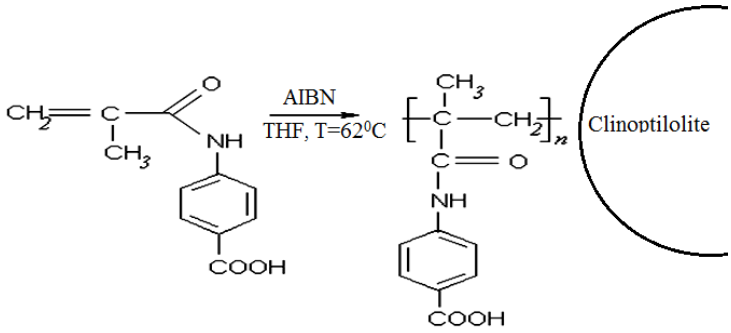


Figure 1. Scheme of polymerization reaction of *N*-(4-carboxyphenyl)methacrylamide on the surface of clinoptilolite

The fact of successful *in situ* polymerization on the surface of clinoptilolite was established by comparative analysis of the IR spectra of the initial (A) and modified (B) minerals, as shown in Figure 2.

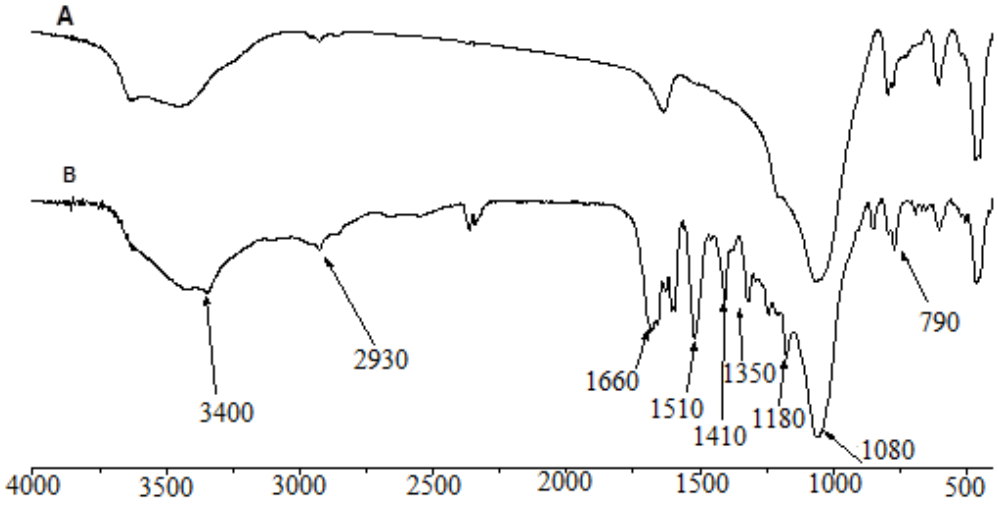


Figure 2. Infrared spectrum of the initial (A) and modified (B) clinoptilolite

In order to determine the mass of the immobilized polymer, a thermogravimetric analysis of the initial and modified clinoptilolite were performed. The obtained thermograms are shown in Figures 3 and 4. From these figures it is seen that the predominant amount of immobilized polymer decomposes in a temperature range of 100 to 510°C. At the same time, about 18% of the weight of the composite is lost, which proofs that it is the exact mass of polymer on the surface of clinoptilolite.

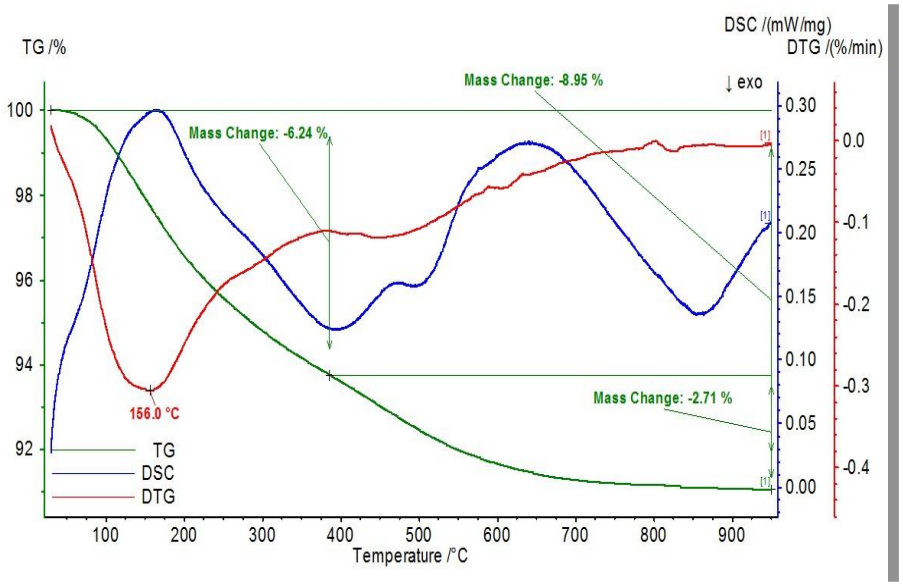


Figure 3. Thermogram of the initial clinoptilolite

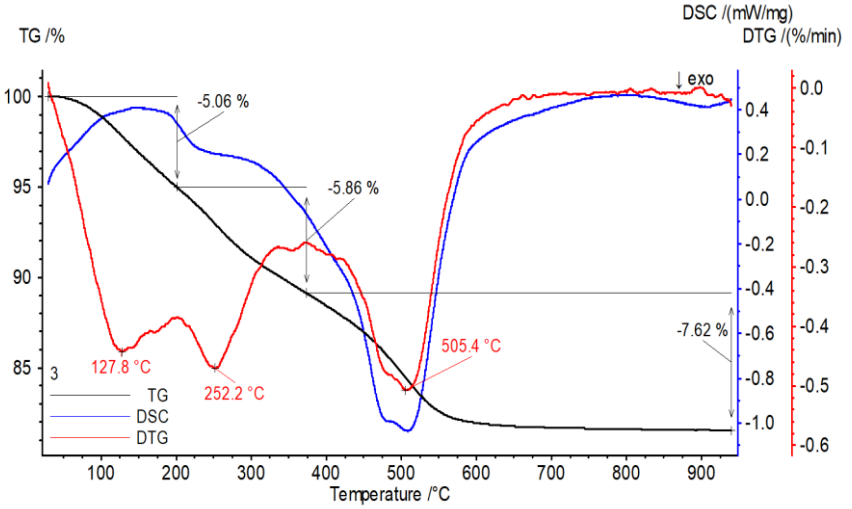


Figure 4. Termogram of modified clinoptilolite

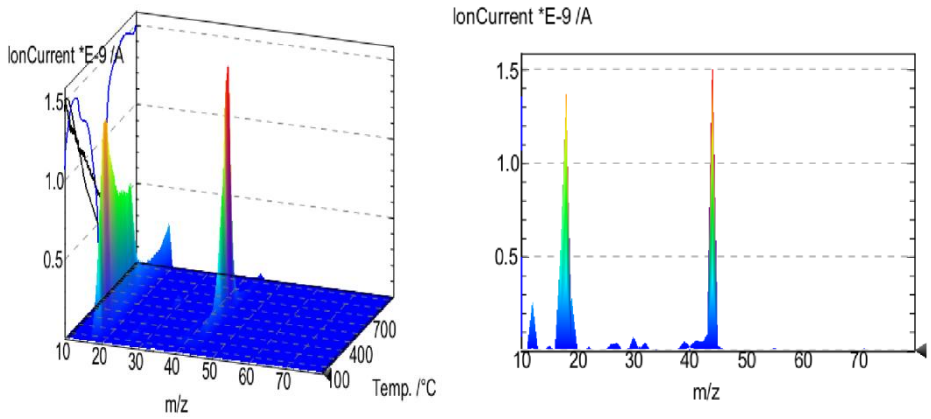
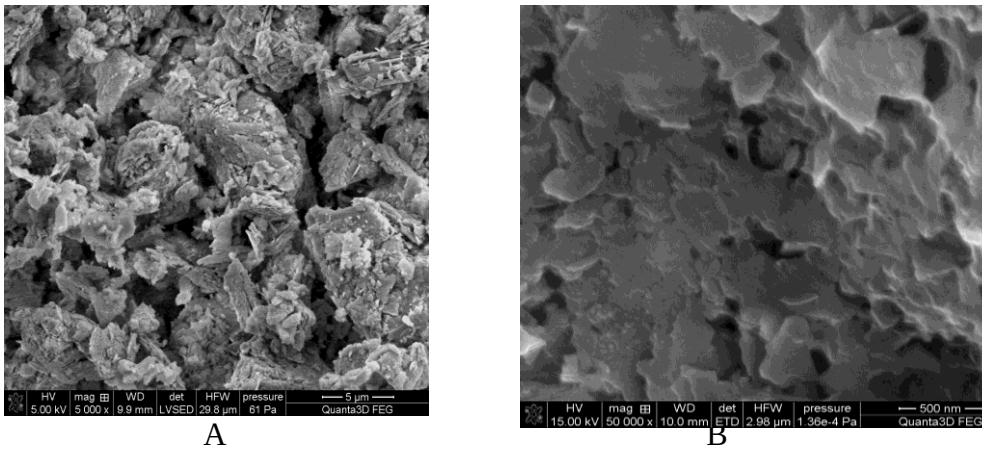


Figure 5. DSC-QMS-3D (A) and QMS-2D(B) of the synthesized composite

Figure 5 shows a thermogram of a synthesized composite combined with a mass spectrum in 3D format and a mass spectrum in 2D format. According to the mass spectrometry, it is evident that, as a result of the thermal degradation of the immobilized polymer, particles of mass 18, 28 and 44 Da are most preferably to form, which most likely correspond to the formation of water, nitrogen, CO_2 and N_2O.

The surface of clinoptilolite before and after modification by a polymer was investigated by scanning electron microscopy (Figure 6). As seen from obtained photos, the polymer on the surface of the mineral is evenly dispersed in the form of a that smoothes the surface of the mineral, reducing the poresize.



A B

Figure 6. SEM images (an increase of 5,000 ×) of sample of the initial (A) and SEM images (an increase of 50,000) of sample of the clinoptilolite polymer modified (B)

Sorption properties of clinoptilolite, in situ modified with poly[N-(4-carboxyphenyl)methacrylamide], in relation to Cu(II), Cd(II), Pb(II), Mn(II), Fe(III) ions

The study of the sorption ability of the synthesized composite related to Cu(II), Cd(II), Pb(II), Mn(II), Fe(III) ions included:

- determination of the optimal pH range of the sorption environment;
- establishing the required contact time of phases to achieve the sorption equilibrium in static mode;
- construction of isotherms of sorption of the corresponding metal ions on the surface of the synthesized composite;
- determination of the sorption capacity for the investigated metal ions and comparison with such for the original mineral.

The results of studies of the sorptive ability of clinoptilolite, *in situ* modified with poly[*N*-(4-carboxyphenyl)methacrylamide], related to Cu(II), Cd(II), Pb(II), Mn(II), Fe(III) ions at various pH levels and composition of chemical environment are shown in Table 1.

The analysis of table 1 shows that clinoptilolite, *in situ* modified with poly[*N*-(4-carboxyphenyl)methacrylamide], exhibits the highest sorption activity relative to the micro-quantity of all the metals studied in a neutral solution. However, as can be seen from this table, the maximum sorption of Fe(III) ions is observed in a weakly acidic medium.

When the solutions of the salts of the investigated metals contacting with the surface of the synthesized composite in a weakly-loop environment created by a $NaHCO_3$ solution (pH 8.1) was observed partial flushing of the immobilized polymer into the liquid phase, and the solution that contacted the sorbent, acquired a yellow color.

Subsequent studies of sorption properties of modified clinoptilolite were carried out with solutions of Cu(II), Cd(II), Pb(II) nitrates without the addition of buffers.

Table 1. Dependence of the degree of sorption of metal ions on the surface of the Tushin clinoptilolite, in situ modified with poly[N-(4-carboxyphenyl)methacrylamide], in relation to pH level of the environment. Conditions of the experiment: m (sorb) = 0.1 g, V solution. = 25 ml, m^0M = 100μg,contact time 24 hours

pH	Degree of sorption, %				
	Pb(II)	**Mn(II)**	**Cu(II)**	**Fe(III)**	**Cd(II)**
4.0	25,53	0	27,07	76,22	0
5.5	100,00	49,25	79,65	30,80	76,26
8.4	0	2,69	68,93	0	0

Figure 7 shows the dependence of the degree of sorption of Cu(II), Cd(II) and Pb(II) ions on the surface of clinoptilolite, *in situ* modified by poly[*N*-(4-carboxyphenyl)methacrylamide], in relation on time in static mode.

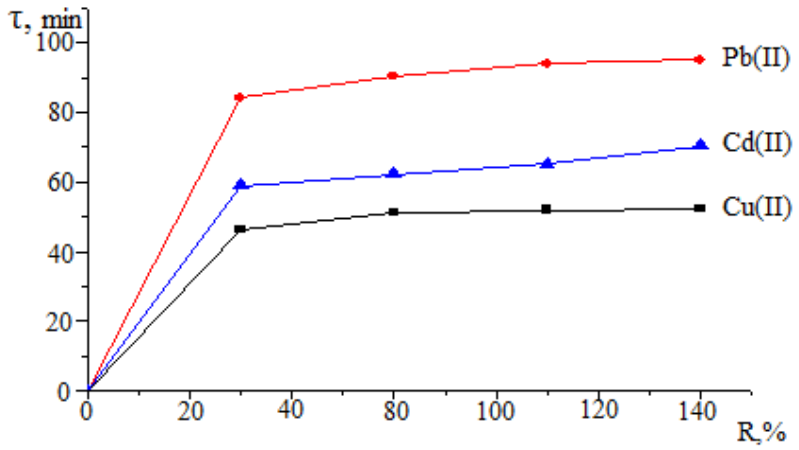


Figure 7. Dependence of degree of sorption of ions Pb (II), Cd (II), Cu (II) to time of contact with synthesized sorbent in static mode

From Figure 7 comes that all studied ions are sorbed within 30 minutes of contact, after which a sorption equilibrium is established, and the change of sorption level is insignificant.

In order to establish the values of the sorption capacity of the modified clinoptilolite in regard to the selected transition metal ions, their isotherms of sorption

were constructed and compared with isotherms of initial (non-modified) clinoptilolite. An example of the sorption isoterms of Cd(II) ions is shown in Figure 8.

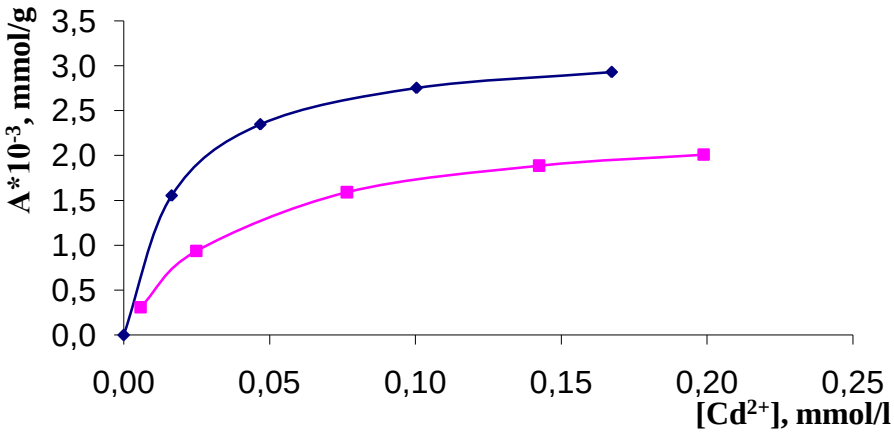


Figure 8. Isotherms of sorption of ions of Cd(II) on unmodified(1) and modified clinoptilolite (2)

According to the obtained isotherms, it is possible to make a preliminary conclusion that the sorptive capacity of clinoptilolite after modification with poly[*N*-(4-carboxyphenyl)methacrylamide] increases and relates to all investigated ions, which is most likely due to complexation processes with nitrogen or oxygen atoms on the immobilized polymer. All the obtained isotherms belongs to the 2L-species, which indicates to the evenly position of the sorbed metal ions on the solid surface of the sorbent (Parfitt & Rochester, 1986).

The sorptive capacity of the modified mineral for each of the investigated transition metal ions, calculated from the data of sorption isotherms, is summarized in table 2. The data of this table suggest that the sorption capacity of clinoptilolite after modification with poly[*N*-(4-carboxyphenyl)methacrylamide] in the molar ratio increases for Pb(II) ions in 1,9 times, in relation to Cd(II) ions by 1,4 times, in relation to Cu (II) ions by 1,8 times.

Table 2. Comparison of sorption capacity modified with poly[N-(4-carboxyphenyl)methacrylamide] and the initial clinoptilolite in relation to Cu(II), Pb(II) and Cd(II) ions

Cation	Sorption capasity			
	Initial clinoptilolite		Modified clinoptilolite	
	mmol/g	mg/g	mmol/g	mg/g
Pb(II)	0,010	1,982	0,019	3,952
Cd(II)	0,022	2,463	0,030	3,345
Cu(II)	0,009	0,576	0,016	1,024

4. Conclusions

A new organo-mineral composite material was obtained by *in situ* immobilization of poly[*N*-(4-carboxyphenyl)methacrylamide] on the surface of Carpathian clinoptilolite (Ukraine). The fact of polymer immobilization is confirmed by IR spectroscopy. By results of TG and DSC-MS analysis was found out that the mass of the immobilized

polymer is 18%. As a result of the comparison of the sorptive properties of the modified and non-modified minerals in relation to the ions Pb(II), Cd(II), Cu(II), Mn(II) and Fe(III) ions, their improvement was recorded after modification by the selected polymer in relation to the ions Pb(II), Cd(II) and Cu(II).

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