



In situ immobilization on the silica gel surface and adsorption capacity of poly[4-methacroyloxy-(4'-carboxy-2'-nitro)-azobenzene] on toxic metals ions

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ABSTRACT

A new organo-mineral composite material has been synthesized by *in situ* immobilization of poly[(4-methacroyloxy-(4'-carboxy-2'-nitro)azobenzene) on the silicagel surface. As a result of thermogravimetric analysis and DSC-MS analysis it has been found that the composition of synthesized composite includes 10,1 wt. % of polymer. It has been found that the synthesized composite exhibits the sorption ability in terms of microquantities of Cu (II), Cd (II), Pb (II) and Fe (III) ions in a neutral aqueous medium. The maximum degree of sorption of ions Cu (II), Pb (II) and Fe (III) is achieved during the first minutes of contact, and for Cd (II) ions the equilibrium is established within a day. The sorption capacity of silica gel as a result of modification by this polymer increases with respect to Cu (II) ions more than 14 times, with respect to Pb (II) ions - 5 times.

KEYWORDS

adsorption; poly [(4-methacroyloxy-(4'-carboxy-2'-nitro)azobenzene; composite; *in situ* immobilization; heavy metals; silica

1. Introduction

Azo compounds are the most common dyes, whose production is more than half of the total production of dyes due to the simplicity and cheapness of synthesis. They are used as stable paints, analytical reagents, phosphors, etc. [1–3]. Both monomeric and polymeric azo compounds are widely known for their interesting complex-forming properties [4, 5].

The modification of the surface of porous inorganic materials by nitrogen-containing polymers allows to obtain sorbents for removing toxic metals from the waste water due to their complexation with nitrogen atoms of immobilized polymer [6–8]. One of the promising ways of creating organo-mineral composite materials with valuable sorption properties is polymerization or *in situ* immobilization, which consists in the direct formation of an immobilized polymeric layer in the presence of particles of inorganic matrix [9–11].

The advantages of this method of fixing a polymer on a solid surface in comparison with physical adsorption of pre-synthesized polymers are optimal location of macromolecules on a solid surface, which strengthens the fixation of a polymer on an inorganic matrix. This arrangement of macromolecules creates additional possibilities for the regeneration of the

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Table 1. Characteristics of the surface of silica gel and synthesized composite

Object of study	Surface area, m ² / g			Average pore volume cm ³ / g	Average pore size, nm
	P/P ₀	BET	Langmuir		
Silica gel	447,00	463,53	686,91	0,686	5,92
synthesized composite	341,00	358,15	539,08	0,570	6,36

obtained composite material as a sorbent in multiple applications, and the possibility of self-organization of polymer chains in supramolecular structures on the surface of an inorganic matrix, the presence of which increases the sorption capacity of the composite. Compared to the chemical bonding of pre-synthesized polymers in situ immobilization is characterized by the absence on the solid surface of the matrix the residues of monomolecular compounds, which were used as bridging groups between the inorganic matrix and the polymer. All this leads to expansion of the range of immobilized polymer adsorption ability and improve its adsorption capacity.

This work is devoted to the *in situ* immobilization of poly[(4-methacroyloxy-(4'-carboxy-2'- nitro)azobenzene] on the silica gel surface, and adsorption properties of the synthesized composite material on ions Pb(II), Cd(II), Cu(II) and Fe(III).

2. Experimental

2.1. Synthesis

For the study, the silica gel produced by Merck ((fraction of particles with a diameter of 0.1-0.2 mm), whose surface parameters are given in Table 1, were used.

The polymerization of 4-methacroyloxy-(4'-carboxy-2'-nitro)azobenzene in the presence of silica gel has been carried out under the argon atmosphere. A solution of 7,73 g [(4-methacroyloxy-(4'-carboxy-2'- nitro)azobenzene] and 0.07 g of 2,2'-azobisisobutyronitrile (AIBN) in 80 ml tetrahydrofuran (THF) were poured into a flask containing 7,73 g of silica gel. When argon blowing was finished after 15 min, the reaction mixture was heated to 68 °C; polymerization continued for 6 hours 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 propanol-2, filtered and air-dried for 24 hours at room temperature.

2.2. Characterization methods.

IR spectra of the original and modified silica gel were recorded using an infrared spectrophotometer "Spectrum BX" (Perkin Elmer, Germany) in the range 500–4000 cm⁻¹ in tablets KBr.

The amount of immobilized polymer on the silica gel surface was evaluated by thermogravimetric analysis results obtained with simultaneous TG/DTA analyzer Shimadzu DTG-60 H (Japan) with computer registration of data in the 15-1000 °C temperature range. The heating rate of samples is 10 °C/min.

Thermal analysis was carried out on a STA 449 Jupiter F1, Netzsch (Germany) with mass spectroscopy console QMS 403C Aeölos (Germany)

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

The morphology of the surface of silica gel before and after modification by polymer was investigated by scanning electron microscopy using the electron microscope “SEM LEO 1430 VP” (Carl Zeiss, Germany).

Sorption characteristics of the synthesized material with respect to Cu (II), Cd (II), Pb (II) and Fe (III) ions were studied in static mode. At the same time, 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, 30, 60, 90 minutes and day with mechanical shaking. The equilibrium concentration of metal ions was fixed by the atomic absorption method.

The working solutions of the nitrates of the selected metals for the study of the sorption properties of the modified silica gel were prepared from the sets of “standard samples of solutions” of these salts (produced by AV Bogatsky, Odessa) on the background of 1 MNNO₃ at concentrations of 1 and 10 mg/ml.

To create a medium with pH 4, a phthalate buffer solution was used from a set of “Standard buffer solutions” (DSTU 8.135: 2009, manufacturer of OJSC “Kiev plant of RIAP”). pH 2.8 was made by adding 0.1 M acetic acid, which was prepared from fixanal. The exact pH of the working solutions was determined using the pH meter “HANNA TESTER WP” (Hanna instrument, China).

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

$$A = (c_o - [M]) V / m$$

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

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

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

where m_o – is mass of metal in the starting solution (mkg), m_{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).

The balanced metal ions concentration was defined by atom-absorption method. Atom-absorption measuring was made with the help flame atom-absorption spectrophotometer “Saturn” (Ukraine) in flame solution “air - propane - butane”. The wavelengths were: for cuprum - 324.7 nm, cadmium - 228.8 nm, plumbum - 283.3 nm, ferum - 248.3 nm, and the width of the crack of 0.58 cm. The balanced concentrations calculations in solution were made by comparing method of their lines intensity in the standard solutions intensity spector. Standard solutions were prepared with metal concentrations of 0.1-1.5 µg/ml.

3. Results and Discussion

The Chemical structure of *in situ* polymer immobilization of 4-methacroyloxy-(4'-carboxy-2'-nitro)azobenzene on the silica surface could be presented as follows (Figure 1):

Infrared spectra of the original (1) and the modified (2) silica gel, are shown in Figure 2.

A comparative analysis of the infrared spectra of the synthesized composite and the original silica gel (Figure 2) shows that in the spectrum of the composite, in contrast to the original matrix, there are new absorption bands in the region from 1401 to 3460 cm^{-1} , which are related to the following vibrations: - at 1401 cm^{-1} , there is a stretching vibrations ν (N=N) bond, characteristic of azo compounds; the absorption band at 1659 cm^{-1} can be attributed to the valence asymmetric vibrations ν_{as} (NO_2); the absorption band at 2343 cm^{-1} can be attributed to the valence vibrations ν (Si-H). Its presence indicates the existence of hydrogen bonds between polymer and silica gel. The absorption bands in the region from 2860 to 3070 cm^{-1} can be attributed to

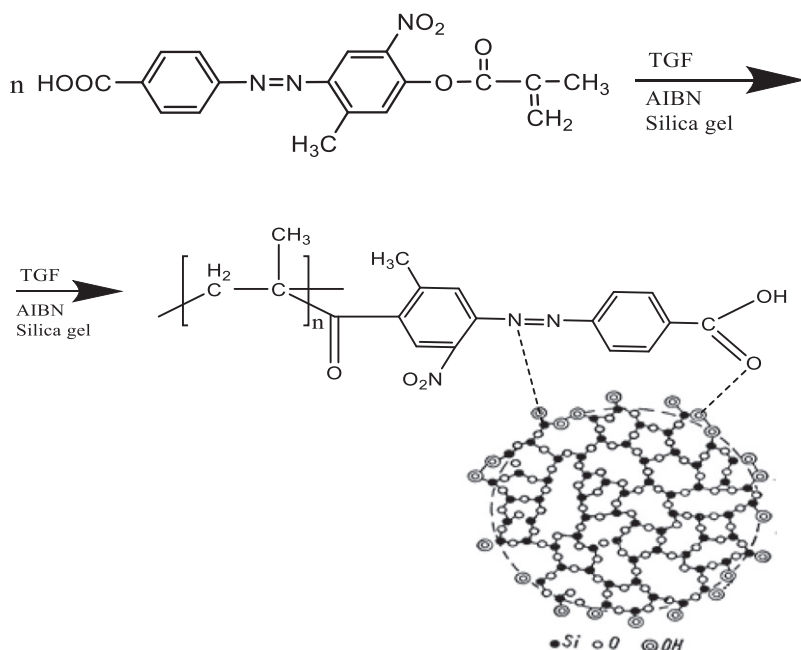


Figure 1. The scheme of *in situ* immobilization of poly[(4-methacroyloxy-(4'-carboxy-2'-nitro)azobenzene on the silica gel surface

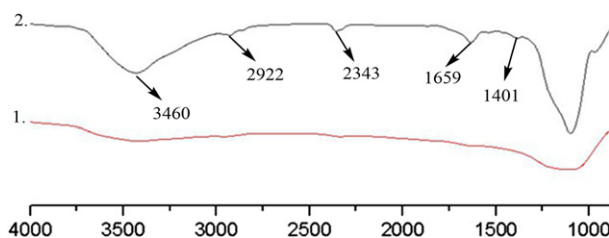


Figure 2. Infrared spectra of the original (1) and the modified (2) silica gel

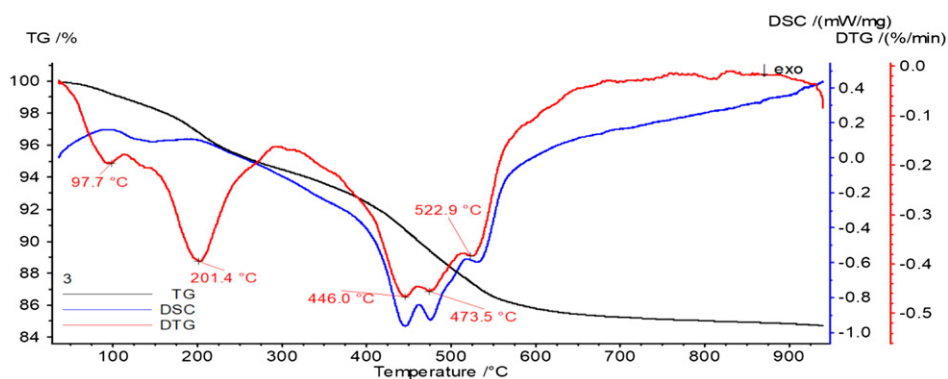


Figure 3. Thermogram of synthesized composite

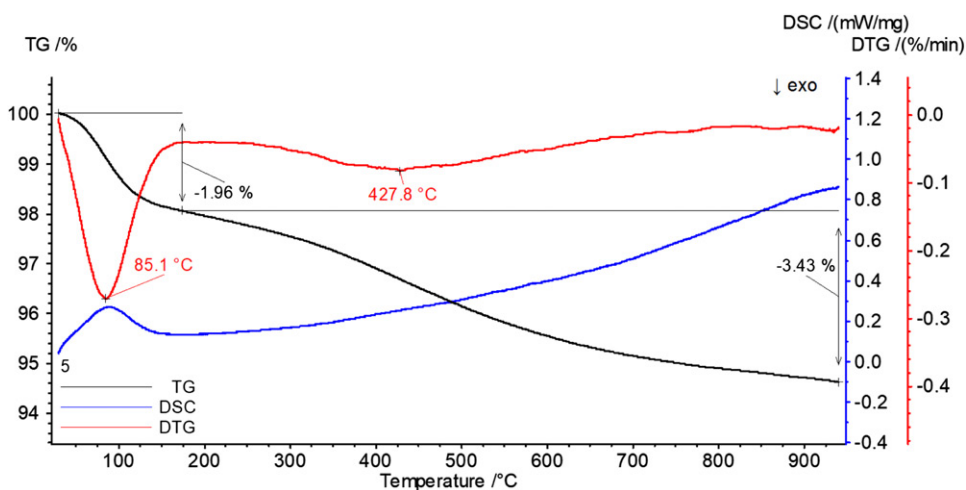


Figure 4. Thermogram of original silica gel

symmetric valence vibrations in groups of ν (CH) sp^3 -hybridized Carbon of polymer chains. Their presence in the spectrum of the composite testifies to the fact that the polymerization reaction proceeds on the surface of the inorganic matrix.

- the absorption band at 3460 cm^{-1} corresponds to the valence vibration of ν (O-H) carboxyl group [12, 13].

Thus, the results of IR spectroscopy confirm the presence of a polymer on the surface of silica gel. In addition, the change of color of the silica gel to orange shows the immobilization of the azopolymer on the surface of the silica gel.

In order to determine the concentration of immobilized polymer, a thermogravimetric analysis of the synthesized composite and the original silica gel was performed. The obtained thermograms are shown in Figures 3 and 4. From Figure 3 it can be seen that the most intense thermodestruction of the composite occurs in the temperature range from 97 to 570°C . At the same time, about 15.5% of the weight of the composite is lost. This loss is due to the destruction of the immobilized polymer and the loss of residual water in the silica gel, which, according to Figure 4, is 5.4%. Consequently, the mass of the immobilized polymer is 10.1%.

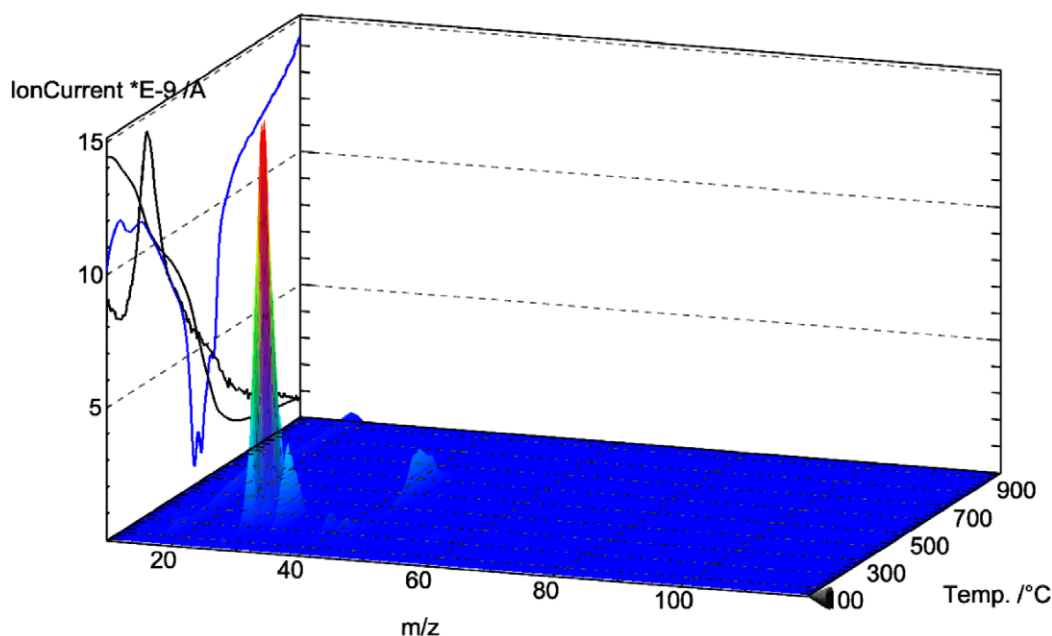


Figure 5. TG-MS-3D of synthesized composite

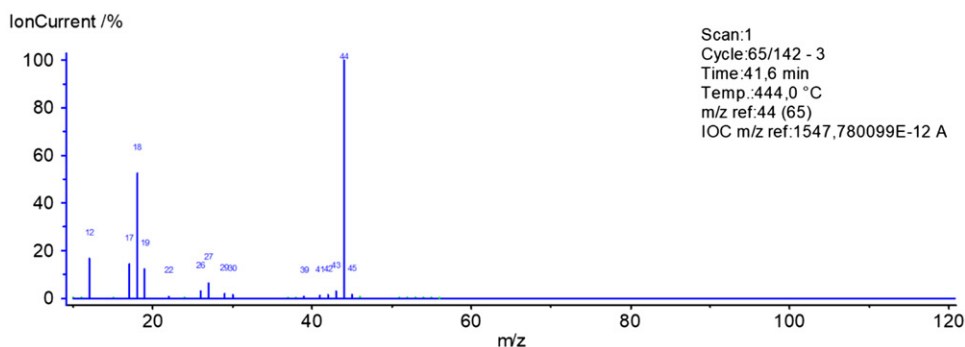


Figure 6. Mass spectrum of the synthesized composite at T 522.4 $^{\circ}$ C.

In order to detail the process of thermodestruction of the composite, a thermogram was obtained which is combined with the mass spectrum in 3D format (Fig. 5) and a number of 2D-mass spectra at temperatures of 98.4 $^{\circ}$ C, 201.3 $^{\circ}$ C, 444, 0 $^{\circ}$ C and 522.4 $^{\circ}$ C (fig. 6).

Interpretation of the data of the obtained mass spectra suggests that the mass loss of the composite occurring at a temperature interval of about 100 $^{\circ}$ C (maximum peak at 97.7 $^{\circ}$ C) is due to the evaporation of residual water in the composition of silica gel, which is confirmed by the presence of a single peak of high intensity at 18 in the mass spectrum at a temperature of 98.4 $^{\circ}$ C.

The next significant mass loss occurs at a temperature of 201.4 $^{\circ}$ C and corresponds to the beginning of the thermal degradation of the immobilized polymer. The presence in the mass spectrum at this temperature of a peak of high intensity with a mass of 26

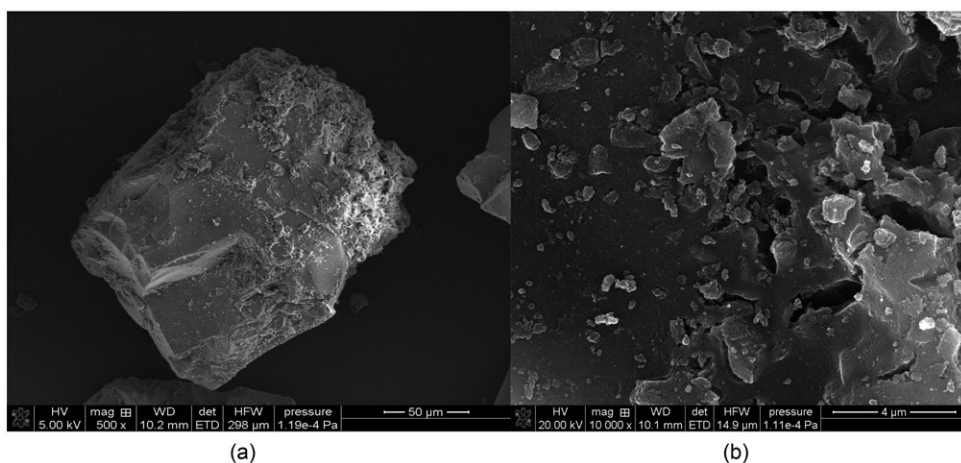


Figure 7. SEM-microphotographs of synthesized composite at 50 000 × (a), 100 000 × (b) magnification

which can be attributed to the formation of the CN groups, and the second peak intensity of 32, which may correspond to the formation of oxygen, indicates that the destruction of the immobilized polymer begins with azo dye.

At higher temperatures (from 420 to 570° C), the thermal degradation of the main carbon chain of the immobilized polymer with the decomposition of its torn chains to carbon dioxide, water, and soot formation occurs. This fact is evidenced by the presence in the mass spectra of the composite at temperatures of 444.0° C, 470.3° C and 522.4° C of the most intense peaks at 44, 18 and 12 (fig.6).

The BET method (low-temperature adsorption-desorption of nitrogen) was used to study the parameters of the silica gel surface after immobilization of poly [4-methacryloxy- (4'-carboxy-2'-nitro) -azobenzene]. The adsorption-desorption nitrogen isotherms for the original silica gel and the synthesized composite are similar and belong to the IV type isotherm according to the classification of IUPAC [14]. Consequently, the structure of the surface of silica gel as a result of fixation of this polymer does not change practically.

The parameters of the surface of the synthesized composite calculated by computer processing of nitrogen adsorption-desorption isotherms are shown in Table 1. The obtained data indicate that after immobilization of the polymer, the porosity of the silica gel surface decreases insignificantly: the surface area decreases from 447 to 341 m²/g, the average pore size decreases from 0.67 to 0.57 cm³/g, while the average diameter of pores increases from 5.92 to 6.36 slightly.

Changes in the surface morphology of silica gel after modification by an azopolymer were followed by scanning electron microscopy (CEM). The CEM-photos of modified silica gel with an increase of 500 and 10,000 times are shown in Figures 7a and 7b, respectively. From the presented photos it is seen that the polymer covers almost half of each particle of silica gel with a fairly even layer.

The synthesized composite should detect the sorption ability of ions of transition metals due to the complex activity of the nitrogen atoms of the azo groups and of the nitro group, as well as of the oxygen atoms of the carboxyl groups of the immobilized

Table 2. Dependence of degree of sorption of ions Cu (II), Cd (II), Pb (II) and Fe (III) on the surface of silica gel, *in situ* modified by poly [4-methacryloxy- (4'-carboxy-2'-nitro) -azobenzene], from the pH and chemical composition of the source solutions. Conditions of the experiment: $m_{\text{sorb}} = 0.1 \text{ g}$, $V_{\text{sol.}} = 25 \text{ ml}$, $m_{0\text{M}} = 100 \mu\text{g}$, contact time - 24 hours.

pH	Degree of adsorption (%)			
	Cu^{2+}	Cd^{2+}	Pb^{2+}	Fe^{3+}
1.2	0,00	0,00	0,00	11,80
2.8	12,91	4,07	39,21	80,90
4.0	18,60	0,00	37,73	37,08
5.5 (dist H_2O)	85,33	64,03	99,99	89,61

polymer. To confirm these considerations, we investigated the sorption of Cu (II) and Fe (III) ions, which have high affinity for nitrogen-containing ligands [12].

Also, sorption of ions of toxic metals such as Cd (II) and Pb (II), which form complexes predominantly with oxygen atoms, was studied [15].

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

- determination of the optimal pH range of the sorption medium;
- establishing the required contact time of phases to achieve the sorption equilibrium in the static mode;
- 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 silica gel.

In the previous experimental studies, it was found that in the alkaline medium, this immobilized polymer is partially washed away from the surface of silica gel, so the study of the sorption properties of the synthesized composite was carried out in an acidic and neutral medium only. At the same time, in the initial solutions of the investigated metals aqua, chloride, acetate or phthalate coordination spheres were formed respectively. In the process of sorption such complexes interacted with the molecules of immobilized polymer with the formation on solid surfaces of multi-ligand complexes. Due to this phenomenon sorption occurred.

The results of investigations of the sorption activity of silica gel, *in situ* modified by poly [4-methacryloxy- (4'-carboxy-2'-nitro) -azobenzene] with respect to Cu (II), Cd (II), Pb (II) and Fe(III) with different values of acidity and different chemical composition of the medium is shown in Table 2.

Analysis of Table 2 allows us to assert that the synthesized composite exhibits the best sorption properties of the micro quantities of the selected ions in the aqueous medium (without the addition of any buffer solutions), where it adsorbs the number of ions of Pb (II) quantitatively and removes all the other ions of metals maximally compared with acidic environment.

The stability constants of the various types of complexes of the same metal formed on a solid surface, depending on the chemical composition of the initial coordination sphere, can vary greatly, which significantly affects the degree of its sorption. For example, as follows from Table 2, the acetate complexes of ferrum (III) (at pH 2.8) are

Table 3. Dependence of the degree of sorption of metals of Cu (II), Cd (II), Pb (II) and Fe (III) ions on the surface of silica gel, *in situ* modified by poly [4-methacryloxy- (4'-carboxy-2'-nitro) -azobenzene] from the time of contact in a static mode. Experimental conditions: mass of sorbent – 0.1 g, volume of solution – 25 ml, m^0_M – 100 μg , the medium of the initial solutions is neutral.

Time, min	Degree of adsorption (%)			
	Cu^{2+}	Cd^{2+}	Pb^{2+}	Fe^{3+}
10	72,18	38,60	99,35	71,03
60	73,49	43,27	99,35	65,11
120	73,75	50,58	99,64	54,83
1440	73,13	53,22	99,94	49,22

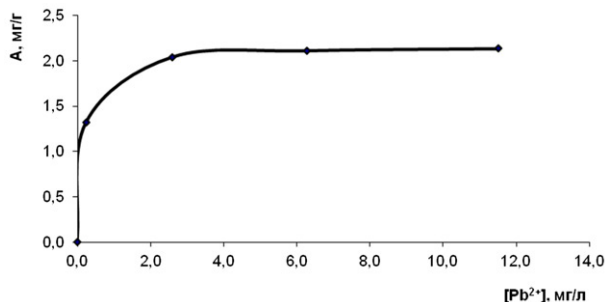


Figure 8. Isotherms for sorption of ions of Pb (II) on the surface of silica gel, *in situ* modified by poly [4-methacryloxy- (4'-carboxy-2'-nitro) -azobenzene].

sorbed on the surface of the synthesized composite by 80%, while phthalate (at pH 4) under the similar experimental conditions is 37% only.

Taking into account all of the foregoing, further investigations of the sorption properties of the modified silica gel were performed with the initial solutions of Cu (II), Cd (II), Pb (II) and Fe (III) nitrates in neutral medium without adding buffers. The dependence of the degree of sorption of Cu (II) ions, Cd (II), Pb (II) and Fe (III) on the surface of silica gel, *in situ* modified by poly [4-methacryloxy- (4'-carboxy-2'-nitro) -azobenzene] are shown in Table 3.

The obtained data testify that the Cu (II) and Pb (II) ions are sorbed as much as possible during the first minutes of contact with the surface of the composite. The degree of sorption of ions Cd (II) increases gradually during the contact time, but 50% of 100 μg of these toxic ions are sorted within an hour of contact in a static mode. The ions Fe (III) are absorb as much as possible during the first minutes of the contact, and then their partial washing from the solid surface is returned to the solution. The reason for this phenomenon may be the low stability of multi-ligand complexes on a solid surface.

In order to determine the values of the sorption capacity of the modified silica gel for the selected transition metal ions, their isotherms of sorption were constructed. Isotherm sorption of ions Pb (II) is shown in Figure 8.

All of the obtained isotherms belong to the 2L-species, which indicates that the sorbed metal ions are distributed evenly on a solid surface of the sorbent. This type of isotherm is typical for silica matrices, modified by complex-forming substances [16].

Table 4. The comparison of sorption capacities for ions Cu (II), Pb (II) and Fe (III), original silica gel and synthesized composites

Cation	Sorption capacity			
	Original silica gel		Modified silica gel	
	mmol / g	mg/g	mmol / g	mg/g
Fe(III)	0,008	0,49	0,0157	0,88
Pb(II)	0,002	0,41	0,0103	2,13
Cu(II)	0,006	0,38	0,0860	5,50

The obtained isotherms allow to calculate the sorption capacity of the synthesized composite. The comparison of the sorption capacitance values of the synthesized composite with respect to Cu (II), Pb (II) and Fe (III), and Cu (III) ions, and the initial silica gel is given in Table 4.

The data in this table suggest that the sorption capacity of silicagel after the modification of poly [4-methacryloxy- (4'-carboxy-2'-nitro) -azobenzene] with respect to Cu (II) ions increases by more than 14 times, with respect to Pb (II) - 5 times, but for ions Fe (III) - 2 times only. Of course, this is the result of immobilization on the surface of the selected polymer, which is capable of participating in complex formation.

4. Conclusions

A new organo-mineral composite material has been synthesized by *in situ* immobilization of poly [4-methacryloxy- (4'-carboxy-2'-nitro) -azobenzene] on the silica gel surface by polymerization of the [4-methacryloxy- (4'-carboxy-2'-nitro) -azobenzene] in the presence of 2,2'-azobisisobutyronitrile as the initiator of radical polymerization.

The fact of heterophase polymerization 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 10,1 wt. % of polymer. The analysis of the CEM photo of the synthesized composite showed that the immobilized polymer on the surface of the silica gel was placed evenly in the form of a thin layer.

As a result of studies on the sorption capacity of the synthesized composite for Cu (II), Cd (II), Pb (II) and Fe (III) ions, it was recorded that the synthesized composite exhibits the best sorption properties relative to the micro-quantities of the selected ions in a neutral aqueous medium (without adding any which types of buffer solutions), where it quantitatively sorbents the micro-quantities of Pb (II) ions and removes maximally all other investigated metal ions compared to the acidic medium.

It was found that the maximum degree of sorption of ions Cu (II), Pb (II) and Fe (III) is achieved during the first minutes of contact, and for Cd (II) ions the equilibrium is established within a day. According to the results of data processing, isotherms of sorption have found that immobilization of the surface of silica gel leads to an increase in its sorption capacity in relation to Cu (II) ions more than 14 times, in relation to Pb (II) ions - 5 times, but for Fe (III) ions - 2 times only.

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